

Utah State University

DigitalCommons@USU

All Graduate Theses and Dissertations

Graduate Studies

5-1970

Magnesium Ion Inhibition of Calcium Carbonate Precipitation and its Relation to Water Quality

John J. Hassett
Utah State University

Follow this and additional works at: <https://digitalcommons.usu.edu/etd>



Part of the [Other Chemistry Commons](#), and the [Soil Science Commons](#)

Recommended Citation

Hassett, John J., "Magnesium Ion Inhibition of Calcium Carbonate Precipitation and its Relation to Water Quality" (1970). *All Graduate Theses and Dissertations*. 4574.

<https://digitalcommons.usu.edu/etd/4574>

This Dissertation is brought to you for free and open access by the Graduate Studies at DigitalCommons@USU. It has been accepted for inclusion in All Graduate Theses and Dissertations by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.



MAGNESIUM ION INHIBITION OF CALCIUM CARBONATE
PRECIPITATION AND ITS RELATION
TO WATER QUALITY

by

John J. Hassett

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Soil Chemistry

Approved:

UTAH STATE UNIVERSITY
Logan, Utah

1970

318-101
1970
C. S.
Bryant, and others

ACKNOWLEDGMENTS

I would like to express my deep appreciation to Dr. Jerome J. Jurinak for his encouragement and helpful guidance during my studies. I sincerely appreciated my acquaintance with him and the chance of working with him.

I would also like to express my thanks to Dr. Raymond L. Kerns, Dr. James W. Sinclair, Dr. R. L. Smith and Dr. Alvin R. Southard for serving as committee members.

This dissertation is dedicated to my wife, Gloria, without her help and sacrifices this dissertation would never have been completed.

John J. Hassett

John J. Hassett

TABLE OF CONTENTS

	Page
INTRODUCTION	1
REVIEW OF LITERATURE	4
Effect of Mg	5
Solution phase	5
Solid phase	7
METHODS AND MATERIALS	9
RESULTS AND DISCUSSION	20
SUMMARY AND CONCLUSIONS	40
PROPOSALS FOR FUTURE WORK	44
LITERATURE CITED	46
APPENDIXES	48
Appendix A. Development of the Carbonate Saturometer Theory after Weyl (24)	49
Appendix B. Calculation of $a_{Ca^{++}}$, $a_{Mg^{++}}$ and $a_{HCO_3^-}$ as Effected by Ion-pair Formation	54
Appendix C. Computer Program	59
VITA	61

LIST OF TABLES

Table	Page
1. Composition of waters (Series 2)	11
2. Composition of waters (Series 1)	12
3. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material	17
4. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material	17
5. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material	18
6. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material	18
7. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material	19
8. Calculation of amount of CaCO_3 dissolved or precipitated	26

LIST OF FIGURES

Figure	Page
1. Reaction vessel	14
2. Change in pH (Δ pH) resulting from addition of T, U, M, P to waters 1	29
3. Δ pH resulting from addition of T, U, M, P to waters 2	30
4. Δ pH resulting from addition of T, U, M, P to waters 3	31
5. Δ pH's resulting from addition of T, U, M, P to waters 4	32
6. Δ pH's resulting from addition of T, U, M, P to waters 5	33
7. Comparison of calculated Δ pH's waters 1 with actual Δ pH(T)	34
8. Comparison of calculated Δ pH's water 2 and actual Δ pH(T)	35
9. Comparison of calculated Δ pH's water 3 and actual Δ pH(T)	36
10. Comparison of calculated Δ pH's waters 4 with actual Δ pH(T)	37
11. Comparison of calculated Δ pH's water 5 with actual Δ pH(T)	38

ABSTRACT

Magnesium Ion Inhibition of Calcium Carbonate

Precipitation and its Relation

To Water Quality

by

John J. Hassett, Doctor of Philosophy

Utah State University, 1970

Major Professor: Dr. Jerome J. Jurinak
Department: Soils and Meteorology

The effect of Mg^{++} ion on the solubility of calcium carbonate was determined using P. K. Weyls "carbonate saturometer."

The amount of calcium carbonate precipitated or dissolved was measured for five series of waters when equilibrated with solid carbonate.

It was found that the effect of Mg^{++} ion on solubility depended upon the nature of the solid phase: surface area, coprecipitated Mg^{++} , minerology, etc.

Pure low area calcite showed an increase in solubility which could be explained by ion-pair formation, while its other carbonates departed from this behavior.

(67 pages)

INTRODUCTION

The precipitation or solution of CaCO_3 in terms of water quality is important. From the industrial and municipal view, the solution of CaCO_3 and MgCO_3 by irrigation return flow waters increases the concentration of Mg^{++} and Ca^{++} ions in solution. Eldridge (11) considers the increase of water hardness due to Ca^{++} and Mg^{++} ions to be the most important single adverse effect contributed by irrigation return flows. Hardness results in increased cost of soap, water softening and boiler scale.

From an agronomic approach CaCO_3 precipitation, while reducing the total salt load of the water, can increase the sodium hazard of the water when used for irrigation purposes. Eaton (10) recognized the potential hazard caused by CaCO_3 precipitation from the irrigation waters when he introduced the concepts of (a) possible sodium percentage and (b) residual sodium carbonate (RSC). These were attempts to estimate the sodium hazard by assuming that all Mg^{++} and Ca^{++} ions in solution would precipitate quantitatively in the presence of excess HCO_3^- and CO_3^{--} ions.

$$\text{Possible sodium percentage} = \frac{\text{Na}^+}{(\text{Na}^+ + \text{Mg}^{++} + \text{Ca}^{++}) - (\text{HCO}_3^- + \text{CO}_3^{--})}$$

$$\text{Residual sodium carbonate} = (\text{CO}_3^{--} + \text{HCO}_3^-) - (\text{Ca}^{++} + \text{Mg}^{++})$$

where () represents concentrations expressed in meq/liter.

Wilcox (25) in field and laboratory studies came to the conclusion that waters with more than 2.5 meq/liter RSC were not suitable for

irrigation purposes. Waters containing 1.25 to 2.5 meq/liter RSC were marginal and those containing less than 1.25 meq/liter RSC were probably safe. Babcock et al. (2) found in a 4-year lysimeter study, using artificial waters, that the amount of exchangeable Na^+ produced did not appear to be closely related to the HCO_3^- in the water. This is in contrast to what might be expected from Eaton's (10) principle of possible sodium percentage.

Langelier (16) devised an index to indicate the extent of waters flowing in a closed system (no loss of CO_2) to precipitate or dissolve CaCO_3 . The saturation index is defined as the actual pH of the water (pHa) minus the theoretical pH (pHc) that the water would have if it were in equilibrium with CaCO_3 (calcite).

$$\text{Saturation index} = \text{pHa} - \text{pHc}$$

Positive values of the index indicate that CaCO_3 will precipitate from the water, whereas negative values indicate that the water will dissolve CaCO_3 . Langelier's equation for the pHc is:

$$\text{pHc} = (\text{pKa}'_2 - \text{pKsp}') + \text{pCa} + \text{pAlk}$$

where pKa'_2 and pKsp' are, respectively, the second dissociation constant and the solubility constant of H_2CO_3 and CaCO_3 corrected for ionic strength. pCa is the negative logarithm of the calcium ion concentration and pAlk is the negative logarithm of the equivalent concentration of titratable base ($\text{CO}_3^{=} + \text{HCO}_3^-$).

Bower (4), and Pratt, Bronson and Chapman (21) found the fraction of applied HCO_3^- that precipitated in the soil was highly related to a modified Langelier saturation index. The modification was the

replacement of the actual pHa of water with the pH of the highly-buffered soil (pHs). The saturation index used was:

$$\text{(Modified) Saturation index} = \text{pHs} - \text{pHc}$$

Bower, Ogata and Tucker (5) further modified the saturation index, to obtain a better fit with experimental data, by replacing pCa with a linear combination of the concentration of magnesium and calcium in the solution, p(Ca + Mg).

$$\text{pHc}^* = (\text{pKa}_2' - \text{pKsp}') + \text{p}(\text{Ca} + \text{Mg}) + \text{pAlk}$$

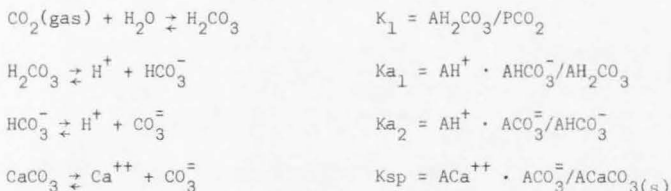
where saturation index = pHs - pHc*.

The above equations assume that the chemical reactions of magnesium are the same as calcium and that $\text{Ca}^{++} + \text{Mg}^{++}$ can be combined in a linear combination to allow for the precipitation of both CaCO_3 and MgCO_3 .

It is the contention of the author that this type of additivity is not valid since (a) MgCO_3 has a greater solubility than CaCO_3 , (b) Mg^{++} ion may inhibit precipitation by interfering with nucleation, (c) Mg^{++} can increase the total amount of CaCO_3 which will dissolve due to the formation of ion-pairs and (d) Mg^{++} can interact with the CaCO_3 crystal forming a more soluble crystal than pure calcite.

REVIEW OF LITERATURE

The solution and precipitation of CaCO_3 are controlled by several variables. Ponnampetuma (20), Garrels and Christ (13) and others give the following equilibria which control simple CaCO_3 systems (Mg^{++} ion absent).



Usually the $\text{ACaCO}_3(\text{s})$ is taken to be unity reducing K_{sp} to:

$$K_{sp} = \text{ACa}^{++} \cdot \text{ACO}_3^{=}$$

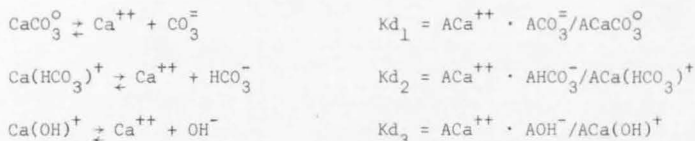
Kern (15) showed that the solution of CO_2 (gas) to give H_2CO_3 is two separate processes. K_1 is the correct value for the equilibrium constant of the first reaction and the value for K_{a1} is a composite of the second process and the value for the first dissociation of carbonic acid.



In addition to these equilibria, the system is complicated by ion-pair formation, which involves the $\text{CO}_3^{=}$, HCO_3^- , OH^- and Ca^{++} ions.

Davies (7) implies that formation of ion-pairs is the result of specific short range interactions which produce soluble, but undissociated, species. The effect of the presence of these ion pairs is to increase the amount of CaCO_3 which will dissolve and to lessen the amount which will precipitate compared to a system without ion-pairs. The equilibrium condition ($K_{sp} = A\text{Ca}^{++} + \text{ACO}_3^-$) still holds for the system, but an increased amount of CaCO_3 must dissolve to meet it.

Important ion-pairs equilibria for a simple CaCO_3 system (Mg^{++} ion absent) are given below:



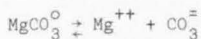
Nakayama (18) found in saturated CaCO_3 solutions, under atmospheric conditions, that 20 percent of the calcium in solution exists as ion-pairs, with CaCO_3^0 being the predominant species.

Effect of Mg

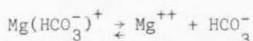
Mg^{++} ion can affect carbonate equilibria by interacting with the solution or the solid phase.

Solution phase

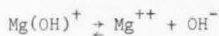
In addition to the ion-pairs involving the Ca^{++} ion, Greenwald (14), Garrels and Christ (13), Davies (7) and others have shown that the Mg^{++} ion can react to form ion-pairs with the same effect on carbonate equilibrium as the Ca^{++} ion, ion-pairs. The important equilibria are listed below:



$$Kd_4 = \text{AMg}^{++} \cdot \text{ACO}_3^- / \text{AMgCO}_3^0$$



$$Kd_5 = \text{AMg}^{++} \cdot \text{AHCO}_3^- / \text{AMg}(\text{HCO}_3^-)^+$$



$$Kd_6 = \text{AMg}^{++} \cdot \text{AOH}^- / \text{AMg}(\text{OH})^+$$

Doner and Pratt (8) found that CaCO_3 precipitated in Ca^{++} and Mg^{++} -saturated montmorillinite suspensions was more soluble than calcite. When CaCO_3 was precipitated from CaCl_2 and NaHCO_3^- in clay suspensions with Mg-saturation as a variable, its solubility was related to the amount of Mg^{++} ion in solution with apparently no effect of the clay per se. Doner and Pratt (9) measured the solubility of CaCO_3 precipitated in the presence of various salts at controlled CO_2 partial pressures. They found that in NaCl solutions the solubility of carbonate precipitated was that of calcite while in MgCl_2 solutions the solubility was higher. In the MgCl_2 solutions, both the aragonite and calcite were detected and Mg^{++} was coprecipitated in the solid phase.

In addition to the effect of Mg^{++} ion-pair formation on CaCO_3 solution or precipitation, Mg^{++} may directly effect calcium carbonate precipitation by inhibiting calcite nucleation.

The formation of a precipitate may be considered to consist of two distinct processes: nucleation and crystal growth. The fact that supersaturated solutions exist for definite periods of time suggests that the process of initiating precipitation differs from the process of continuing precipitation once it has been initiated. Fisher (12) states that the distinction between the two processes results from the fact that the force in crystal growth is the overcoming of hydration energy by lattice energy, while in the nucleation process no lattice and hence no lattice energy exists. There exists, therefore,

an energy barrier to nucleation which must be overcome before crystallization can occur. One result of the energy barrier is the development of various degrees of solution supersaturation prior to crystallization.

The effect of Mg^{++} ion on $CaCO_3$ nucleation was first recognized by Leitmeir (17) who found that Mg^{++} ion favored the precipitation of aragonite over calcite. Bischoff (3) found that Mg^{++} ion inhibited the diagenetic aragonite-calcite transformation by reacting with calcite nuclei. Since the dehydration of the reactants on the surface of growing crystals is often the rate controlling step, Bischoff (3) postulated that Mg^{++} ion being more strongly hydrated than Ca^{++} remains hydrated when it reacts with the calcite nuclei and thus inhibits further growth. This inhibition is overcome when sufficient nuclei have been formed to remove the Mg^{++} ion to a level at which new nuclei can form which do not contain Mg^{++} ion. Pytkowicz (22) found that Mg^{++} ion inhibited the precipitation of $CaCO_3$ from sea water by forming $MgCO_3$ complexes, thus making more collisions necessary to initiate precipitation.

Solid phase

Mg^{++} ion can affect carbonate equilibrium by interacting with the solid phase as well as the solution phase. Akin and Lagerwerff (1) reported enhanced solubility of $CaCO_3$ precipitating from supersaturated solutions in the presence of Mg^{++} and SO_4^{--} ions. He developed a theory of enhanced solubility based on the Langmuir adsorption of Mg^{++} and SO_4^{--} ions, and the ions of $CaCO_3$ on a crystal surface consisting of calcite and $CaCO_3$ having a modified crystal lattice.

Weyl (24) found that he could not explain the slow kinetics he found for calcite dissolution in the presence of Ca^{++} and Mg^{++} ions by ion-pair formation and concluded that the rate inhibiting mechanism was at the solid-liquid interface. He also found that 1 m mole of Mg^{++} per kilogram of solvent can increase solubility approximately 12 percent over pure calcite.

Chave and Schmalz (6) found using pH-sensing techniques that three factors involving the solid phase, mineralogy, grain size and character, control the interaction of the carbonate crystal with the associated water. He also found the activities of magnesium calcites were four times greater than pure calcite and that particles of calcite 10^{-6} cm in diameter have activities more than eight times greater than 1 cm particles.

METHODS AND MATERIALS

The determination of the state of CaCO_3 equilibrium is complicated by the number of variables which cannot be experimentally measured. Attempts to use thermodynamic-derived constants for the various equilibria require correction for ion-pair formation, ionic strength and deviation of the activity of the solid phase from its standard state of unit activity.

It was decided because of these difficulties that the method developed by Weyl (24) would be used as a measure of carbonate solubility. Weyl (24) developed the "carbonate saturometer" which makes it possible to measure the degree of departure of most aqueous solutions from saturation with respect to a particular solid carbonate. The method is based upon the fact that the pH of a solution changes as the $\text{CO}_3^{=}$ ion is added or removed from solution. If a water sample is undersaturated with respect to a solid CaCO_3 , CaCO_3 dissolved produces $\text{CO}_3^{=}$ ions which combine with H^+ ions increasing the pH of the solution. If the water is supersaturated with respect to a solid CaCO_3 , CaCO_3 precipitates, HCO_3^- ions dissociate and the pH decreases. If the water is saturated with respect to a solid CaCO_3 , the pH of the suspension remains the same.

The "carbonate saturometer" is calibrated by comparing the amount of strong acid or base required to produce the same change in pH (ΔpH) that results when a standard addition of HCO_3^- is made.

$$F(x) = z/y$$

where z equals the amount of strong acid (+ z) or base (- z) required to produce the same ΔpH as y moles of bicarbonate and $F(x)$ is a function of the hydrogen ion activity:

$$F(x) = (1 + 2K_a'_2/x)/(1 + x/K_a'_1 + K_a'_2/x) - 1$$

Once the function $F(x)$ is determined for a water, the water can be equilibrated with a solid CaCO_3 and the ΔpH results noted. Comparison of this ΔpH with the amount of standard acid or base required to produce the same ΔpH and with the function $F(x)$ allows calculation of the amount of CaCO_3 which will dissolve in a given water, if y' equals the number of moles of CaCO_3 which dissolve then:

$$-y = z/(1 - F(x)).$$

A detailed development of the "carbonate staurometer" is presented in Appendix 1.

Experiments were initiated to show the effect of Mg^{++} on CaCO_3 precipitation and solution from unsaturated and slightly supersaturated waters. These experiments consisted of two series of waters (Table 1 and 2). In the first series (Table 1), equal amounts of Ca^{++} and HCO_3^- were added. The degree of saturation was varied by increasing the amounts of Ca^{++} and HCO_3^- equally. Mg^{++} ion concentration was varied from 0M to $2 \times 10^{-3}\text{M}$ and the ionic strength was held constant by addition of NaCl. In the second series (Table 2) Ca^{++} ion concentration was held constant and the degree of saturation varied by increasing the amount of HCO_3^- added. Mg^{++} ion concentration was varied from 0M to $2 \times 10^{-3}\text{M}$ and the ionic strength was held constant

Table 1. Composition of waters (Series 2)

Water	Calcium Conc M	HCO Conc M	Mg Conc M	Ionic Strength (I)
1a	5×10^{-4}	5×10^{-4}	0	.05
1b	5×10^{-4}	5×10^{-4}	5×10^{-5}	.05
1c	5×10^{-4}	5×10^{-4}	2.5×10^{-4}	.05
1d	5×10^{-4}	5×10^{-4}	5×10^{-4}	.05
1e	5×10^{-4}	5×10^{-4}	1×10^{-3}	.05
1f	5×10^{-4}	5×10^{-4}	2×10^{-3}	.05
4a	1×10^{-3}	1×10^{-3}	0	.05
4b	1×10^{-3}	1×10^{-3}	5×10^{-5}	.05
4c	1×10^{-3}	1×10^{-3}	2.5×10^{-4}	.05
4d	1×10^{-3}	1×10^{-3}	5×10^{-4}	.05
4e	1×10^{-3}	1×10^{-3}	1×10^{-3}	.05
4f	1×10^{-3}	1×10^{-3}	2×10^{-3}	.05
5a	2×10^{-3}	2×10^{-3}	0	.05
5b	2×10^{-3}	2×10^{-3}	5×10^{-5}	.05
5c	2×10^{-3}	2×10^{-3}	2.5×10^{-4}	.05
5d	2×10^{-3}	2×10^{-3}	5×10^{-4}	.05
5e	2×10^{-3}	2×10^{-3}	1×10^{-3}	.05
5f	2×10^{-3}	2×10^{-3}	2×10^{-3}	.05

Table 2. Composition of waters (Series 1)

Water	Calcium Conc M	HCO Conc M	Mg Conc M	Ionic Strength (I)
1a	5×10^{-4}	5×10^{-4}	0	.05
1b	5×10^{-4}	5×10^{-4}	5×10^{-5}	.05
1c	5×10^{-4}	5×10^{-4}	2.5×10^{-4}	.05
1d	5×10^{-4}	5×10^{-4}	5×10^{-4}	.05
1e	5×10^{-4}	5×10^{-4}	1×10^{-3}	.05
1f	5×10^{-4}	5×10^{-4}	2×10^{-3}	.05
2a	5×10^{-4}	1×10^{-3}	0	.05
2b	5×10^{-4}	1×10^{-3}	5×10^{-5}	.05
2c	5×10^{-4}	1×10^{-3}	2.5×10^{-4}	.05
2d	5×10^{-4}	1×10^{-3}	5×10^{-4}	.05
2e	5×10^{-4}	1×10^{-3}	1×10^{-3}	.05
2f	5×10^{-4}	1×10^{-3}	2×10^{-3}	.05
3a	5×10^{-4}	5×10^{-3}	0	.05
3b	5×10^{-4}	5×10^{-3}	5×10^{-5}	.05
3c	5×10^{-4}	5×10^{-3}	2.5×10^{-4}	.05
3d	5×10^{-4}	5×10^{-3}	5×10^{-4}	.05
3e	5×10^{-4}	5×10^{-3}	1×10^{-3}	.05
3f	5×10^{-4}	5×10^{-3}	2×10^{-3}	.05

by addition of NaCl. Waters (1, 2 and 4) were undersaturated, while waters (3 and 5) were supersaturated.

Four solid carbonate materials, Mallinckrot reagent CaCO_3 lot TEJ (T), Purecal U (U), Millville soil (M) and Portnuef soil (P), were equilibrated with the waters.

T and U were shown by x-ray diffraction techniques to be pure calcite. Surface measurements using stearic acid adsorption after the method of Suito, Masafumi and Arakawa (23) showed T to be a low surface area CaCO_3 ($\sim .8 \text{ m}^2/\text{gm}$) and U to be a high surface area CaCO_3 ($\sim 13.5 \text{ m}^2/\text{gm}$).

Millville soil is a highly calcareous soil ($\sim 45\% \text{ CaCO}_3$ equivalent) from Utah State Agricultural Experiment Station's north farm. X-ray diffraction showed the calcareous nature to be predominately dolomitic in nature, with a small amount of calcite present.

Portnuef soil is a calcareous ($\sim 20\%$) loess soil from the Snake River Valley in southwestern Idaho. X-ray diffraction showed the calcareous material to contain about equal amounts of calcite and dolomite.

A detailed description of the experimental method is presented below.

- A. Prepare two liters of water by addition of the appropriate amounts of $.1\text{m NaCl}$, $.1\text{m NaHCO}_3$, $.1\text{m CaCl}_2$ and $.1\text{m MgCl}_2$.
- B. NaOH or HCl titration
 1. Pipette 100 ml sample into reaction vessel (Figure 1).
 2. Aerate to constant pH, record pH.
 3. Flush atmosphere above water with N_2 , establish a slight pressure gradient of N_2 between reaction vessel

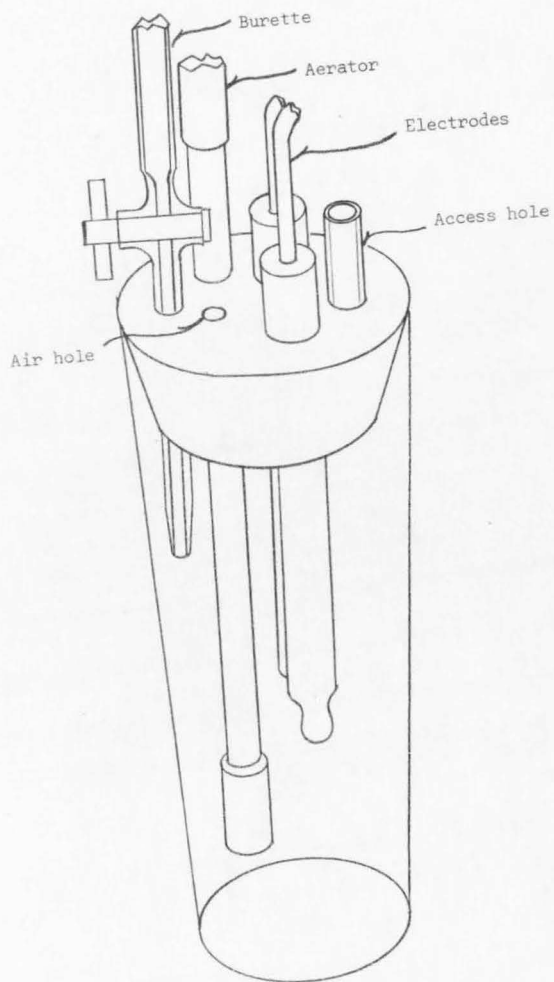


Figure 1. Reaction vessel

and atmosphere.

4. Add .25 ml increments of $\sim 2 \times 10^{-3}$ N NaOH or HCL from burette, allowing pH to stabilize between readings.
5. Record pH resulting from addition of each increment.
6. Plot the titration curve; equivalents/liter vs. Δ pH.

C. NaHCO_3 titration

1. Aerate a new 100 ml subsample to a constant pH, record pH.
2. While aerating add .5 ml increments of 1×10^{-2} M NaHCO_3 to undersaturated samples, .5 ml increments of 1×10^{-1} M NaHCO_3 to supersaturated samples allowing pH to stabilize between readings.
3. Record Δ pH that results from addition of each increment.
4. From the base or acid titration curve determine the equivalents/liter of base or acid required to produce the same pH as results from addition of each increment of bicarbonate.
5. Determine $F(x)$

$$F(x) = \frac{Z}{y}$$

Acid-bicarbonate comparison

D. Solid CaCO_3 addition

1. Aerate a new sample of water to a constant pH, record pH.
2. Add excess of solid CaCO_3 .
3. Aerate to a constant pH, record Δ pH.
4. From titration curves with NaOH or HCl (part B) determine the equivalents/liter of acid or base required to produce

same ΔpH as resulted from the addition of solid CaCO_3 .

5. Calculate

$$-y' = z/(1 - F(x))$$

Where y' equals the number of moles of CaCO_3 which dissolved.

For these experiments, a Heath pH recording electrometer Model EU-301A was used to obtain the necessary pH measurements. The instrument is capable of five full scale pH spans of 1, 2, 5, 10 and 14. For these experiments a pH span of 2 was used, with a lower index setting of 8 for supersaturated waters. The accuracy of the instrument is better than 0.5% full-scale (better than 0.01 pH on a span of 2). For these experiments, the standard deviation (σ) was found to range from $\sigma = .017$ to $\sigma = .01$ depending on the saturation waters. Tables 3, 4, 5, 6 and 7 give $F(x)$ and its standard deviation.

Table 3. $F(x)$ and the amount of CaCO_3 dissolved upon addition of carbonate material

Water 1	$F(x) \pm \sigma_s$	$T \times 10^5$ moles/L	$U \times 10^5$ moles/L	$M \times 10^5$ moles/L	$P \times 10^5$ moles/L
a	$-.0167 \pm .001$	1.35	1.62	.35	1.44
b	$-.0121 \pm .001$	1.33	1.58	.51	1.39
c	$-.0235 \pm .002$	1.50	1.85	.68	1.55
d	$-.0224 \pm .001$	1.52	1.83	.67	1.50
e	--	--	--	--	--
f	$-.0216 \pm .001$	1.75	2.27	.65	1.70

Table 4. $F(x)$ and the amount of CaCO_3 dissolved upon addition of carbonate material

Water 2	$F(x) \pm \sigma_s$	$T \times 10^5$ moles/L	$U \times 10^5$ moles/L	$M \times 10^5$ moles/L	$P \times 10^5$ moles/L
a	$-.0308 \pm .002$	1.21	1.89	.335	1.58
b	$-.0311 \pm .001$	1.36	1.87	.24	1.51
c	$-.0269 \pm .001$	1.28	1.67	.087	1.41
d	$-.0257 \pm .001$	1.49	1.74	.19	1.16
e	--	--	--	--	--
f	$-.0297 \pm .002$	1.6	2.25	.11	1.35

Table 5. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material

Water 3	F(x) \pm os	T $\times 10^5$ moles/L	U $\times 10^5$ moles/L	M $\times 10^5$ moles/L	P $\times 10^5$ moles/L
a	-.0324 \pm .001	5.62	3.95	.96	2.13
b	-.0339 \pm .002	3.38	4.45	.58	2.13
c	-.0349 \pm .001	4.29	6.11	1.9	1.35
d	-.0361 \pm .002	4.34	5.40	2.9	2.27
e	--	--	--	--	--
f	-.0370 \pm .002	4.98	5.80	3.0	2.20

Table 6. F(x) and the amount of CaCO_3 dissolved upon addition of carbonate material

Water 4	F(x) \pm om	T $\times 10^5$ moles/L	U $\times 10^5$ moles/L	M $\times 10^5$ moles/L	P $\times 10^5$ moles/L
a	-.0268 \pm .006	.589	1.22	.098	.852
b	-.0273 \pm .003	.676	1.22	.175	.99
c	-.0291 \pm .003	.557	1.57	.155	1.011
d	-.0281 \pm .001	.593	1.29	.146	.758
e	-.0231 \pm .001	.43	1.07	.049	.332
f	-.0289 \pm .001	.57	1.32	0.00	.65

Table 7. $F(x)$ and the amount of CaCO_3 dissolved upon addition of carbonate material.

Water S	$F(x) \pm \sigma_m$	$T \times 10^5$ moles/L	$U \times 10^5$ moles/L	$M \times 10^5$ moles/L	$P \times 10^5$ moles/L
a	$-.0315 \pm .003$	5.18	4.27	.04	.46
b	$-.0354 \pm .003$	4.94	4.06	.16	.94
c	$-.0315 \pm .002$	4.25	3.75	.00	.47
d	$-.0384 \pm .004$	4.98	3.97	.16	1.21
e	$-.0380 \pm .003$	4.56	4.46	.31	1.01
f	$-.0362 \pm .003$	3.02	4.31	.95	.86

RESULTS AND DISCUSSION

The results of the "carbonate saturometer" experiments for waters 1, 2, 3, 4 and 5 are presented in Tables 3 to 7. The columns going from a to f are at constant ionic strength and constant initial Ca^{++} and HCO_3^- concentrations, but increasing in Mg^{++} ion concentration from 0M to 2×10^{-3} M.

Water 1 (Table 3), the least saturated of the waters with respect to CaCO_3 , shows that with increasing amounts of Mg^{++} ion initially present an increase in the amount of carbonates dissolved occurred in all four carbonate systems (T, U, M, P). The amount dissolved was of the order $U > P > T > M$, for T the solubility of CaCO_3 increased from 1.35×10^{-5} moles/liter to 1.75×10^{-5} moles/liter, with a similar increase with the other solid carbonates.

For water 2 (Table 4) the solid carbonates T and U showed an increase in the solubility with increasing initial Mg^{++} ion concentration, while the soil materials M and P showed a decrease in the amount of carbonate dissolved.

Water 3 (Table 5) was supersaturated with respect to all four calcareous materials. For T, a decrease in the amount of carbonate precipitated resulted upon increasing the initial concentration Mg^{++} . This can be shown to be in agreement with the effect of Mg^{++} ion on waters 1 and 2. For U and the soil materials M and P, an increase in the amount of carbonate precipitated occurred upon increasing the initial concentration of Mg^{++} .

Water 4 (Table 6) was an undersaturated water with the least

potential to dissolve CaCO_3 . It followed the same pattern of water 2 (Table 4) except for water 4 the solubility of T and U was essentially constant as the Mg^{++} concentrate increased.

Water 5 (Table 7) was the most supersaturated water in respect to CaCO_3 . The solubility pattern with regard to increasing Mg^{++} ion concentration also followed that of water 3 (Table 5).

The above results can be explained by considering the nature of the solid carbonates present. Reagent grade calcite (T), a low surface area material ($\sim .8 \text{ m}^2/\text{gm}$), behaved as predicted if only ion-pair formation is considered. Ion-pair formation should result in an increase of the amount of CaCO_3 dissolved by undersaturated water and a decrease in the amount precipitated from supersaturated water. This was found to be the case for T in all waters.

Purecal U (U), a high surface area calcite ($\sim 13.5 \text{ m}^2/\text{gm}$), behaved similar to T when it was equilibrated with undersaturated waters. Purecal U was found to have a higher solubility than T; this was probably due to its higher surface area. Chave and Schmalz (6) found that particles of calcite 10^{-6} cm in diameter had activities more than eight times greater than particles of 1 cm diameter. Equilibration of U with supersaturated waters did not result in a decrease of precipitation with increasing initial Mg^{++} ion concentration as was the case with T, but precipitation was found to increase with increasing concentration of Mg^{++} initially present.

One explanation for this behavior is that Purecal U, a high surface area calcite, is capable of adsorbing sufficient Mg^{++} ion from solution to allow a low area, less soluble calcite to precipitate. This is supported by the fact that the solubility of U decreased to a

value close to the solubility of the low surface area calcite (T).

Another possibility is the replacement of Ca^{++} by Mg^{++} at the crystal surface, producing a solution of higher supersaturation and resulting in increasing precipitation.

Both M and P are calcareous soils. The calcareous material in M is predominately dolomite, while P contains about equal amounts of both calcite and dolomite. When M and P were equilibrated with water 1 (Table 3), they behaved similarly to T and U in that more solid carbonate dissolved as Mg^{++} ion was increased. Upon equilibration of water 2 (Table 4) and water 5 (Table 6) the amount dissolved decreased. This difference is explained by the difference in the saturation of the waters.

Water 1 was sufficiently undersaturated with CaCO_3 that increasing the initial amounts of Mg^{++} ion initially present resulted only in additional ion-pairs being formed, thus increasing the solubility of the carbonate present. While in water 2 and water 4, which are closer to saturation, increasing the initial amounts of Mg^{++} resulted in a decrease in the amount dissolved and an increase in the amount precipitated probably due to the common ion effect of Mg^{++} on dolomite present in the soils. The same explanation can be used to explain the results with the supersaturated waters 3 and 5.

Comparison of the results obtained from the "carbonate saturoometer" experiments with those predicted by a theoretical approach requires the ability to predict the affect of Mg^{++} ion on calcite solution or precipitation.

If Mg^{++} ion concentration only affects the calcite equilibrium by ion-pair formation, the following treatment can be applied. For

systems containing OH^- , HCO_3^- and CO_3^{--} as the only complexing species the total Ca_t , total Mg_t and total HCO_{3t} can be written as:

$$\text{Ca}_t = [\text{Ca}^{++}] + [\text{Ca}(\text{HCO}_3)^+] + [\text{CaCO}_3^0] + [\text{CaCOH}^+] \quad (1)$$

$$\text{Mg}_t = [\text{Mg}^{++}] + [\text{Mg}(\text{HCO}_3)^+] + [\text{MgCO}_3^0] + [\text{Mg}(\text{OH})^+] \quad (2)$$

$$\begin{aligned} \text{HCO}_{3t} = & [\text{HCO}_3^-] + [\text{CO}_3^{--}] + [\text{H}_2\text{CO}_3] + [\text{Ca}(\text{HCO}_3)^+] + [\text{Mg}(\text{HCO}_3)^+] \\ & + [\text{CaCO}_3^0] + [\text{MgCO}_3^0] \end{aligned} \quad (3)$$

where brackets [] represent concentrations.

If the development given in Appendix 2 for $a\text{Ca}^{++}$, $a\text{Mg}^{++}$, and AHCO_3^- is followed, we obtain:

$$a\text{Ca}^{++} = \text{Ca}_t / \left[\frac{1}{\gamma\text{Ca}^{++}} + \frac{\text{K}\text{K}\text{a}_1\text{P}\text{C}\text{O}_2}{\text{Kd}_2\text{A}\text{H}^+\gamma\text{HCO}_3^-} + \frac{\text{Kw}}{\text{Kd}_3\text{A}\text{H}^+\gamma\text{HCO}_3^-} + \frac{\text{K}\text{K}\text{a}_1\text{K}\text{a}_2\text{P}\text{C}\text{O}_2}{\text{Kd}_1(\text{A}\text{H}^+)^2} \right] \quad (4)$$

and

$$a\text{Mg}^{++} = \text{Mg}_t / \left[\frac{1}{\gamma\text{Mg}} + \frac{\text{K}\text{K}\text{a}_1\text{P}\text{C}\text{O}_2}{\text{Kd}_4\text{A}\text{H}^+\gamma\text{HCO}_3^-} + \frac{\text{Kw}}{\text{Kd}_5\text{A}\text{H}^+\text{HCO}_3^-} + \frac{\text{K}\text{K}\text{a}_1\text{K}\text{a}_2\text{P}\text{C}\text{O}_2}{\text{Kd}_6(\text{A}\text{H}^+)^2} \right] \quad (5)$$

and

$$\begin{aligned} \text{AHCO}_3^- = & \text{HCO}_{3t} / \left[\frac{1}{\gamma\text{HCO}_3^-} + \frac{\text{K}\text{a}_2}{\gamma\text{CO}_3^{--}\text{A}\text{H}^+} + \frac{\text{A}\text{H}^+}{\text{K}\text{a}_1} + a\text{Ca}^{++} \left(\frac{1}{\text{Kd}_2\gamma\text{HCO}_3^-} + \frac{\text{K}\text{a}_2}{\text{A}\text{H}^+\text{Kd}_1} \right) \right. \\ & \left. + a\text{Mg} \left(\frac{1}{\text{Kd}_3\gamma\text{HCO}_3^-} + \frac{\text{K}\text{a}_2}{\text{A}\text{H}^+\text{Kd}_4} \right) \right] \end{aligned} \quad (6)$$

These equations can now be used to predict the pH and $a\text{CO}_3^{--}$ of the waters. The $a\text{CO}_3^{--}$ along with the $a\text{Ca}^{++}$ given above in equation (4) can

be used to predict the amount of CaCO_3 (calcite precipitated or dissolved).

Appendix 3 gives the computer program used for this calculation. Briefly the program entails the use of HCO_3^- to predict the pH from the following equations:

$$\text{pH} = \text{pKa}_1 + \log \text{AHCO}_3^- - \log \text{KPCO}_2 \quad (7)$$

This pH is used to calculate aCa^{++} , aMg^{++} and then aHCO_3^- from equations (4, 5 and 6), the aHCO_3^- value is then substituted for HCO_3^- to recalculate the pH. The values of aCa^{++} , aMg^{++} , and aHCO_3^- are recalculated using the new pH value. The iteration sequence is repeated until constant values for pH, aHCO_3^- , aCa^{++} , and aMg^{++} are obtained. The value of $\text{aCO}_3^{=}$ is obtained from:

$$\text{ACO}_3^{=} = \text{Ka}_2 \cdot \text{AHCO}_3^- / \text{AH}^+ \quad (8)$$

Once the value of $\text{aCO}_3^{=}$ and aCa^{++} for the water are known, a function (EE) is calculated:

$$(\text{EEKSP}) = \text{ACa}^{++} \cdot \text{ACO}_3^{=} \quad (9)$$

or

$$\text{EE} = (\text{EEKSP}) / \text{KSP} \quad (10)$$

If $\text{EE} = 1$ then the water is in equilibrium with calcite, if $\text{EE} > 1$ the water is supersaturated and if $\text{EE} < 1$ then the water is undersaturated.

After obtaining the value of EE, the program calculates the amount of CaCO_3 precipitated or dissolved in the following manner.

(a) The original state of the water results in:

$$\gamma\text{Ca}^{++}[\text{Ca}^{++}]\gamma\text{CO}_3^{\ominus}[\text{CO}_3^{\ominus}] = (\text{EEKSP}) \quad (11)$$

(b) At equilibrium the following condition will hold:

$$\gamma\text{Ca}^{++}[\text{Ca}^{++} + \chi]\gamma\text{CO}_3^{\ominus}[\text{CO}_3^{\ominus} + \chi] = \text{KSP} \quad (12)$$

where χ = amount of CaCO_3 that precipitates ($-\chi$) or the amount that dissolved ($+\chi$).

Equating (11) and (12) we obtain:

$$\gamma\text{Ca}^{++}\gamma\text{CO}_3^{\ominus}[\text{Ca}^{++} + \chi][\text{CO}_3^{\ominus} + \chi] = \gamma\text{Ca}^{++} \frac{\gamma\text{CO}_3^{\ominus}[\text{Ca}^{++}][\text{CO}_3^{\ominus}]}{\text{EE}} \quad (13)$$

simplifying

$$\text{EE}\chi^2 + \text{EE}\chi([\text{CO}_3^{\ominus}] + [\text{Ca}^{++}]) + (\text{EE} - 1)([\text{Ca}^{++}][\text{CO}_3^{\ominus}]) = 0 \quad (14)$$

χ can then be determined by solving equation (14), using the quadratic equation.

Table 8 presents EE and the predicted amounts of CaCO_3 which dissolved or precipitated from the various waters.

Comparison of Table 8 with Tables 3 and 7 shows that the theoretical method used here consistently predicts \sim twice as much CaCO_3 dissolved or precipitated as was measured. The method further does not predict the market effect upon adding Mg^{++} ion to the waters as was measured. It is felt that the equations which predict the effect of Mg^{++} on $a\text{Ca}^{++}$, $a\text{Mg}^{++}$, $a\text{CO}_3^{\ominus}$ etc. are valid. The disagreement between the predicted and measured value probably lies in the way χ , the amount of CaCO_3 dissolved or precipitated, was calculated.

An additional comparison can be made between the change in pH (ΔpH) that resulted upon equilibration of the waters 1, 2, 3, 4 and 5

Table 8. Calculation of amount of CaCO_3 dissolved or precipitated

Water 1	EE	χ (moles/L)
a	.0840	4.434x10
b	.0839	4.434x10
c	.0836	4.435x10
d	.0832	4.436x10
e	.0824	4.439x10
f	.0809	4.445x10
Water 2		
a	.302	3.57x10
b	.301	3.57x10
c	.300	3.58x10
d	.298	3.59x10
e	.295	3.602x10
f	.288	3.63x10
Water 3		
a	2.294	-7.337x10
b	2.292	-7.337x10
c	2.283	-7.335x10
d	2.271	-7.33x10
e	2.263	-7.31x10
f	2.263	-7.31x10

Table 8. Continued

Water 4	EE	χ (moles/L)
a	.558	1.216×10^{-5}
b	.557	1.217×10^{-5}
c	.555	1.23×10^{-5}
d	.552	1.236×10^{-5}
e	.546	1.246×10^{-5}
f	.535	1.275×10^{-5}
Water 5		
a	2.813	2.95×10^{-5}
b	2.809	2.947×10^{-5}
c	2.798	2.92×10^{-5}
d	2.783	2.89×10^{-5}
e	2.755	2.89×10^{-5}
f	2.700	2.74×10^{-5}

with the four solid carbonates and those predicted by the saturation index. For the purpose of these comparisons, the actual pH of the water was replaced by the pH predicted for each water by the computer program in Appendix 2.

Figures 2, 3, 4, 5 and 6 give the actual ΔpH 's that resulted upon equilibration of the waters 1, 2, 3, 4 and 5 with the solid carbonates (T, U, M and P).

Figures 7, 8, 9, 10 and 11 give the comparison between the actual ΔpH of CaCO_3 (T) and those predicted by:

$$\text{pHcal} - \text{pHc}$$

$$\text{pHcal} - \text{pHc}^*$$

$$\text{pHcal} - \text{pHc}^{\circ}$$

Where pHcal is the pH predicted by the program in Appendix 2, and pHc

$$\text{pHc} = (\text{pKa}'_2 - \text{pKsp}) + \text{pCa} + \text{pAlk}$$

is defined by Langelier (16), and pHc^* is pHc

$$\text{pHc}^* = (\text{pKa}'_2 - \text{pKsp}) + \text{p}(\text{Mg} + \text{Ca}) + \text{pAlk}$$

as modified by Bower et al. (5) and:

$$\text{pHc}^{\circ} = 5.994 - \frac{2}{3} \log \text{PCO}_2 + \frac{1}{2} (\log \gamma\text{HCO}_3^- - \log \gamma\text{Ca}^{++})$$

where pHc° is the pH of a water open to the atmosphere as derived by Ponnampertuma (20).

The difference between pHc, pHc^* and pHc° is that pHc and pHc^* were derived for closed systems (no CO_2 exchange with the atmosphere),

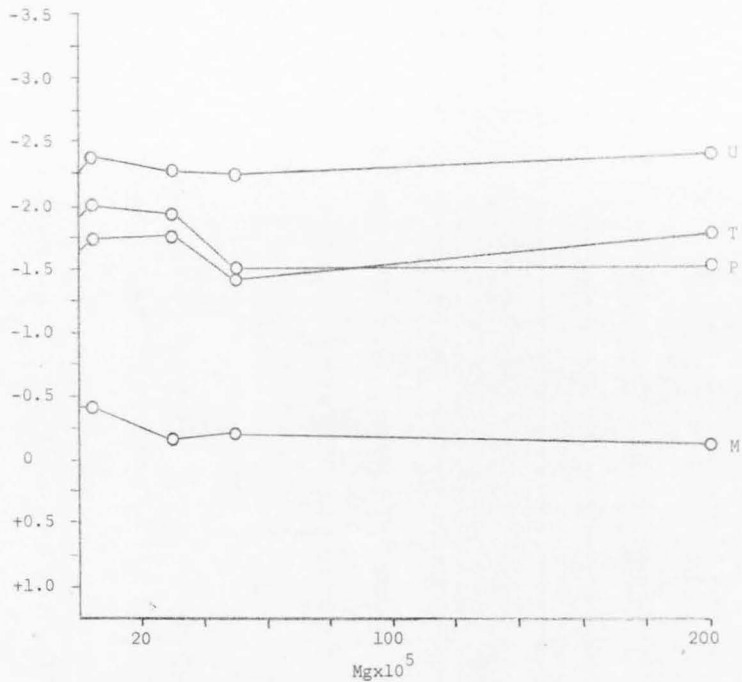


Figure 3. ΔpH resulting from addition of T, U, M, P to waters 2.

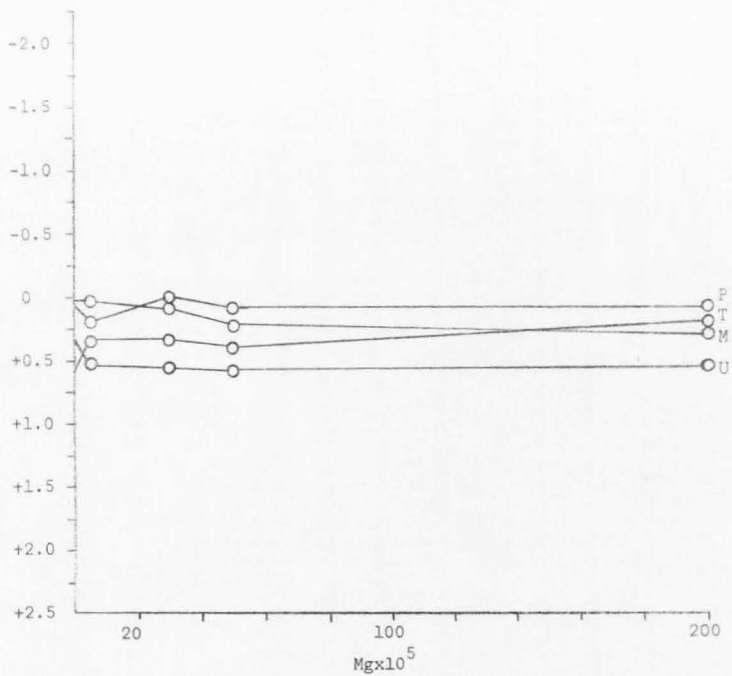


Figure 4. ΔpH's resulting from addition of T, U, M, P to waters 3.

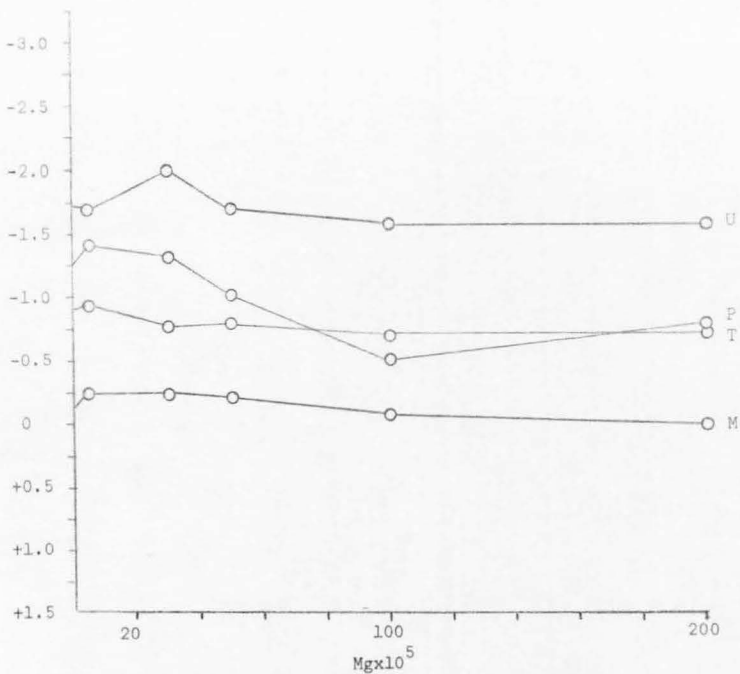


Figure 5. Δ pH's resulting from addition of T, U, M, P to waters 4.

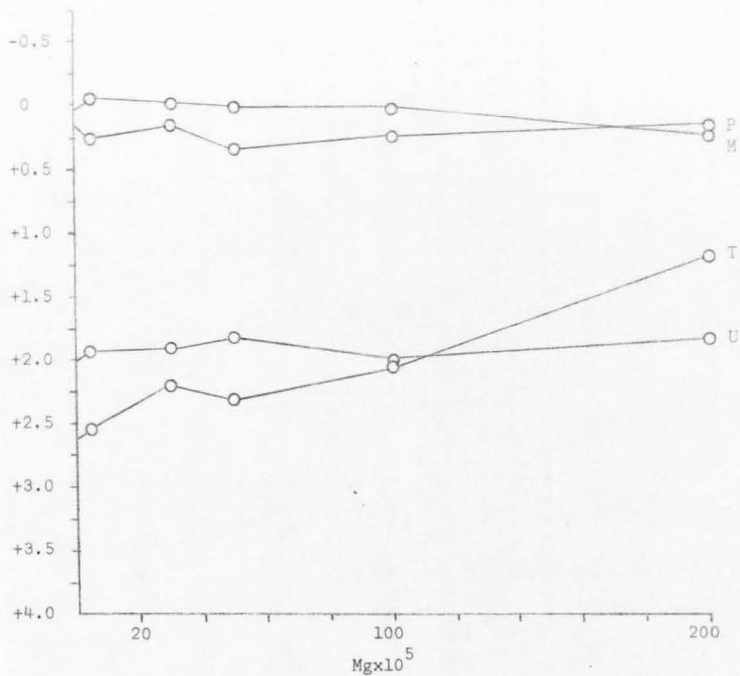


Figure 6. Δ pH's resulting from addition of T, U, M, P to waters 5.

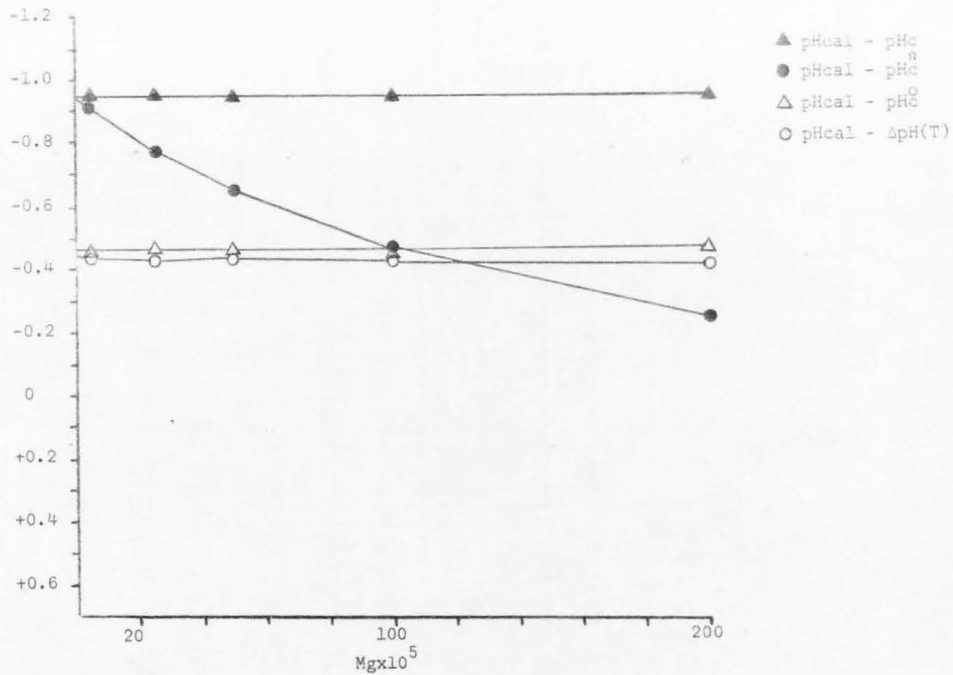


Figure 7. Comparison of calculated ΔpH's waters 1 with actual ΔpH(T).

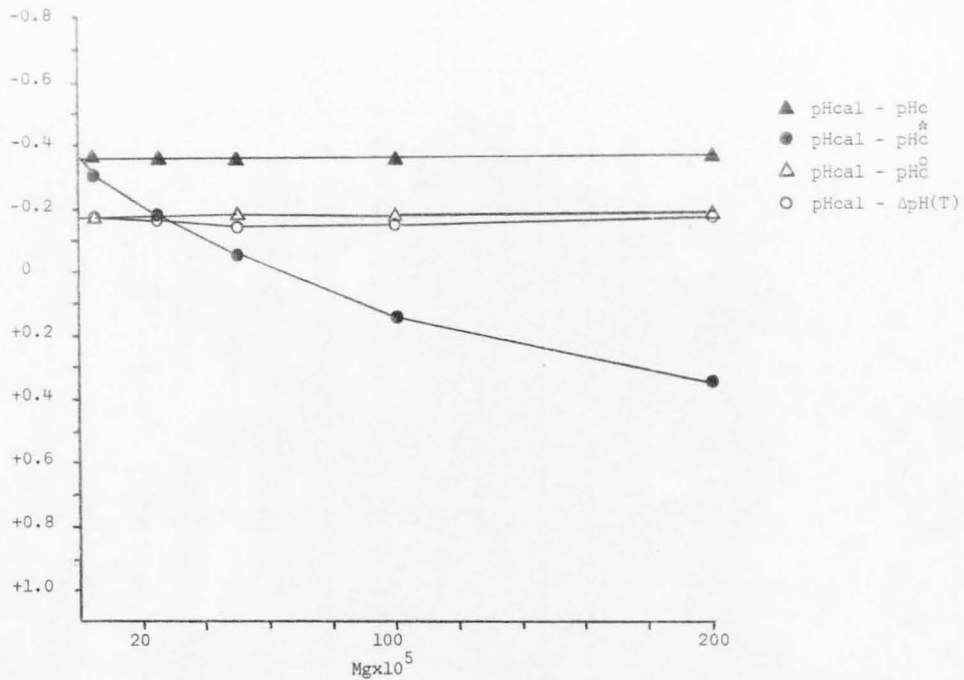


Figure 8. Comparison of calculated ΔpH 's water 2 and actual $\Delta pH(T)$.

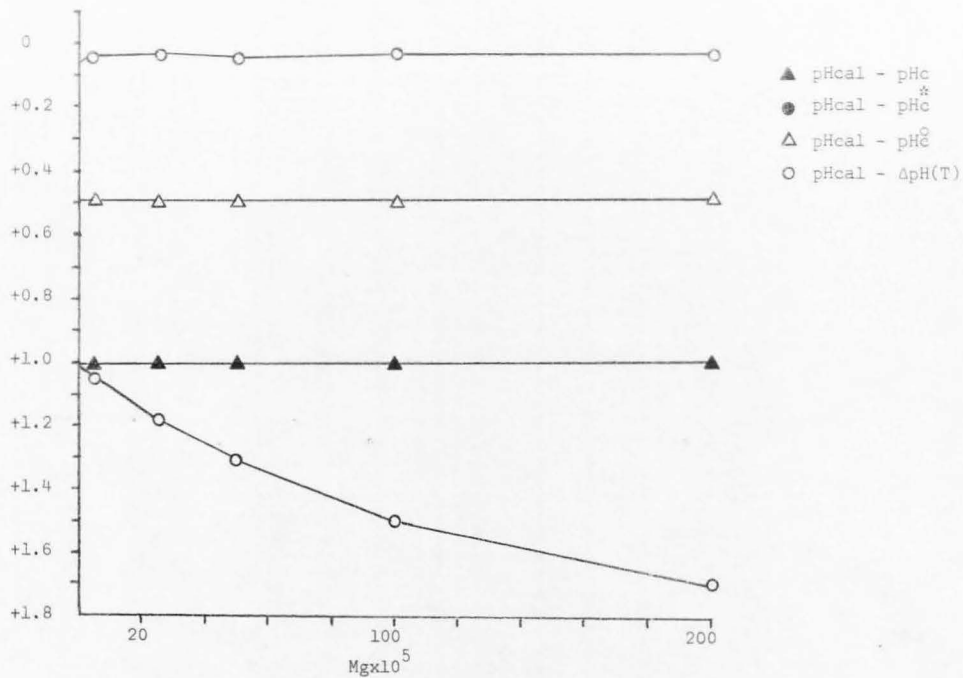


Figure 9. Comparison of calculated ΔpH's water 3 and actual ΔpH(T).

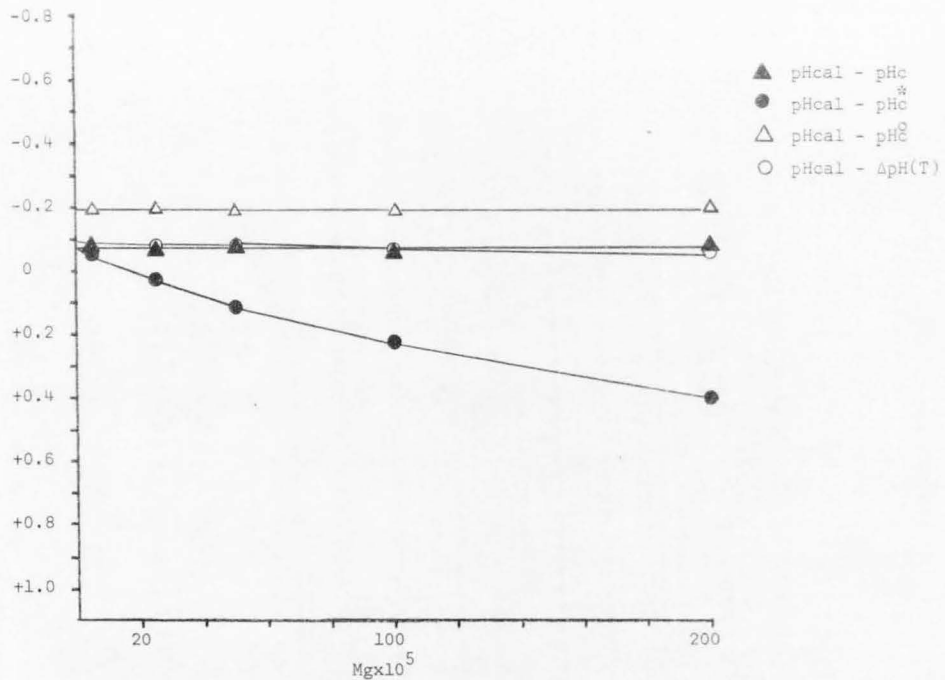


Figure 10. Comparison of calculated ΔpH 's waters 4 with actual $\Delta pH(T)$.

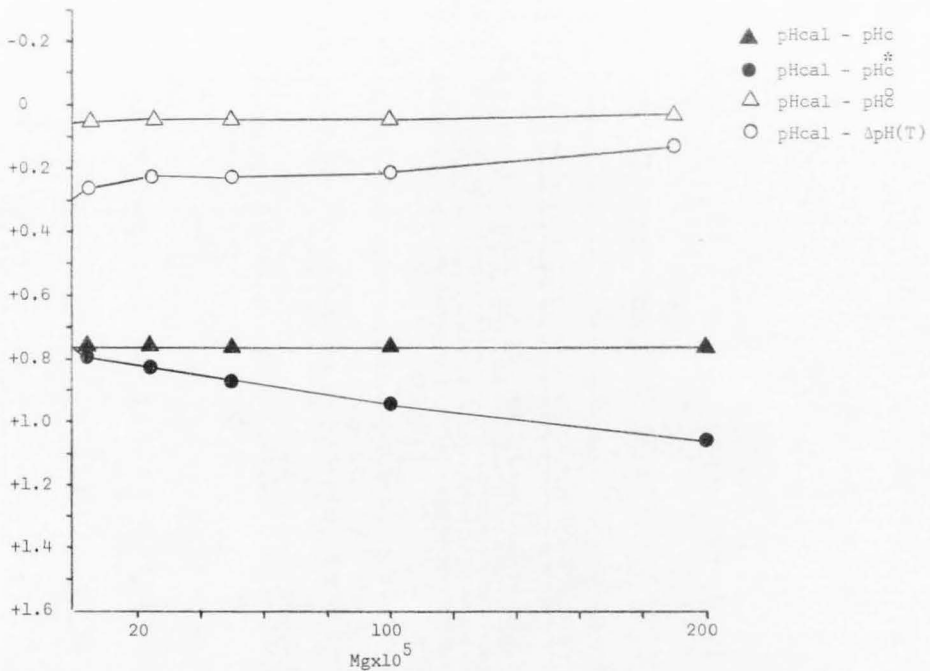


Figure 11. Comparison of calculated ΔpH 's water 5 with actual $\Delta pH(T)$.

whereas pH_C^O was derived for a water open to the atmosphere (open system). The difference between pH_C and pH_C^* is that pH_C^* attempts to correct for the presence of Mg^{++} ion in solution by combining Mg with Ca as $p(Ca + Mg)$.

Examination of Figures 7, 8 and 10 for undersaturated waters 1, 2 and 4 shows that the best and most consistent agreement between the actual ΔpH and a predicted ΔpH is obtained with $pH_{cal} - pH_C^O$. $pH_{cal} - pH_C$ shows the same trend as the actual ΔpH but the magnitude does not agree as well. The worst fit is obtained by the comparison of actual ΔpH with $pH_{cal} - pH_C^*$. $pH_{cal} - pH_C^*$ does not follow the same trend as the actual ΔpH and even predicts that precipitation will take place. See Figures 3, 8 and 10 where actually no precipitation takes place.

Examination of Figures 9 and 11 for supersaturated waters 3 and 5 again shows that the best fit is consistently obtained by comparison of actual ΔpH and $pH_{cal} - pH_C^O$. $pH_{cal} - pH_C$ and especially $pH_{cal} - pH_C^*$ predict considerably more precipitation than actually occurs. The poor fit between actual ΔpH and $pH_{cal} - pH_C$ (Figure 9) is probably due to the high amount of HCO_3^- present ($5 \times 10^{-3} M$) and the small amount of Ca^{++} ($5 \times 10^{-5} M$). This results in a low amount of precipitation taking place and thus a small ΔpH result.

SUMMARY AND CONCLUSIONS

Four different calcareous materials were equilibrated with series of waters of different degrees of saturation with respect to calcite. Within each series of waters, were waters at constant ionic strength and constant Ca^{++} and HCO_3^- concentration, but increasing in Mg^{++} ion concentration. The effect of Mg^{++} ion on the equilibrium position was measured by the "carbonate saturometer" developed by Weyl (24).

It was demonstrated that the nature of the solid phase present, as well as the composition of the solution, can effect the solution and precipitation of calcareous materials. It was demonstrated, in agreement with Chave and Schmalz (6), that high surface area calcites (~ 13.5 m/gm) are more soluble than low surface area ($\sim .8$ m/gm) calcites. Both the high and low surface area calcites showed the similar increases in solubility due to increased Mg^{++} ion when they were equilibrated with unsaturated waters.

Equilibration of the low surface area calcite with supersaturated waters resulted in a decrease in precipitation with increasing Mg^{++} ion concentration, while the high surface area material showed an increase in precipitation. The results for the low surface area calcite when equilibrated with unsaturated or supersaturated waters and the results for the equilibration of high surface area calcite with unsaturated waters, can be explained by the formation of Mg ion-pairs or the adsorption of Mg on the calcite crystal or both.

Solubilities of the calcareous soil materials M and P when equilibrated with very unsaturated waters increased due to ion-pair

formation as the calcite materials did. When M and P were equilibrated with waters which were close to saturation or were supersaturated, a decrease in solubility was noted. This decrease in solubility was explained by the common ion effect of Mg^{++} ion on the solid phase dolomite present in the soils.

A method was developed to predict the effect of Mg^{++} ion-pair formation on calcite equilibrium. The predictions were compared with the experimental values obtained from the saturometer. While the correct trend was predicted by the theoretical treatment, the amount precipitated or dissolved was consistently higher than the actual amounts measured. The predicted effect of increased Mg^{++} ion on $CaCO_3$ equilibrium was considerably less than the actual measured effect.

The theoretical treatment considered only the effect of Mg on calcite equilibrium due to the formation of $Mg(HCO_3)^+$ and $MgCO_3^0$ ion-pairs. The effects of Mg^{++} due to the adsorption of Mg^{++} on the crystal surface or due to coprecipitation of Mg^{++} with the calcite were not considered and they are probably important to quantitative prediction.

Coprecipitation of Mg^{++} with the calcite crystal or the interaction of Mg^{++} with the surface of the calcite crystal, if the processes are separable, would have the same effect as ion-pair formation. Both would increase the amount of $CaCO_3$ dissolved by undersaturated waters. The effect of both adsorbed and coprecipitated Mg would be to decrease the amounts of calcite precipitated from supersaturated waters, but the mechanisms would be different. Coprecipitation results in Mg rich calcites, which would have higher solubilities than pure calcite, while interaction of Mg^{++} with the

surface of the crystal, due to the strong hydration energy of Mg^{++} compared to Ca^{++} , "poisons" sites to further precipitation. Upon dehydration of the adsorbed Mg^{++} , the Mg^{++} could be incorporated into the crystal allowing precipitation to proceed.

A comparison was made between the actual ΔpH that resulted when reagent grade calcite (T) was equilibrated with the waters and the ΔpH predicted by theoretical approaches.

The theoretical equations chosen were:

$$pH_{cal} - pH_c$$

$$pH_{cal} - pH_c^*$$

$$pH_{cal} - pH_c^O$$

where pH_{cal} is the calculated pH of the waters before equilibration with calcite, pH_c is the theoretical pH of a "closed" water (no CO_2 exchange) when equilibrated with calcite as derived by Langelier (16), pH_c^* is the theoretical pH of a "closed" water as modified by Bower (4) to include Mg, and pH_c^O is the theoretical pH of an "open" water (CO_2 exchange occurs) of a water in equilibrium with calcite.

For all waters used in these experiments, the best and most consistent fit was obtained for the comparison of $pH_{cal} - pH_c^O$ and the actual ΔpH .

In conclusion it was demonstrated that for waters far enough removed from saturation with respect to any solid carbonate the effect of increasing the concentration of Mg^{++} ion in solution will be to increase the amount of carbonate dissolved. As saturation is approached and exceeded, if the solid phase does not contain Mg, then

the effect of added Mg^{++} will be to increase solution of and decrease the precipitation of that carbonate. If the solid phase contains Mg to any extent, the effect of added Mg^{++} will be to decrease solution and increase precipitation of that carbonate due to the common ion effect of Mg^{++} on that solid phase.

It was demonstrated that the theoretical equations based on closed systems are not as effective as the equations based on open systems for predicting precipitation or solution of carbonates from or by waters.

It was also shown that the addition of Ca and Mg in predictive equations is not a valid operation when considering precipitation or solution of $CaCO_3$ from waters. If these equations hold for soils, then it is due to the concentration of water in the soil profile by evapotranspiration processes.

PROPOSALS FOR FUTURE WORK

The value of the "carbonate saturometer" to water quality research lies in its ability to measure quantitatively the amount of carbonate which precipitates or dissolves when a certain water is used for irrigation. Of greater value to water quality research would be the development of a method which would allow the prediction of the amount of carbonate precipitated or dissolved from irrigation waters.

Before these predictive equations can be formulated, certain questions need to be answered.

1. What is the range in solubility of the calcareous fraction of soils?
2. How does surface area, degree of crystallinity and coprecipitation effect this range?
3. What effect does CO_2 production by actively growing crops have on solubility?

It is proposed that in order to answer these questions the following experiments be performed.

1. Column experiments
 - a. Set up columns using different calcareous soils.
 - b. Leach the columns with three waters; an undersaturated water, a saturated water and a supersaturated water, at a set leaching fraction (L.f) $\sim .5$.
 - c. Establish degree of saturation using the carbonate saturometer before and after leaching. Analyze Ca^{++} , Mg^{++} , total Alk, EC.

2. Lysimeter experiments

- a. Repeat the column experiments in 5 gallon drums, in which an actively growing crop has been established.

With the above data develop an empirical equation, using regression techniques, to predict the amount of carbonate precipitated or dissolved from or by a given irrigation water.

LITERATURE CITED

1. Akin, G. W., and J. V. Lagerwerff. 1965. Calcium carbonate equilibria in solutions open to the air. II Enhanced solubility of CaCO_3 in the presence of Mg^{++} and SO_4 . *Geochim et Cosmochim. Acta* 29:253-360.
2. Babcock, K. L., M. R. Carlson, R. K. Schulz, and R. Overstreet. 1959. A study of the effect of irrigation water composition on soil properties. *Hilgardia* 29:155-164.
3. Bischoff, J. L. 1968. Kinetics of calcite nucleation magnesium ion inhibition and ionic strength catalysis. *Journal of Geophysical Research* 73:3315-3322.
4. Bower, C. A. 1961. Prediction of the effect of irrigation on soils. *Proceedings UNESCO Arid Zone Symposium, Salinity Problems in the Arid Zones*. Tehran, Iran. p. 215-222.
5. Bower, C. A., G. Ogata, and J. M. Tucker. 1968. Sodium hazard of irrigation waters as influenced by leaching fraction and by precipitation or solution of calcium carbonate. *Journal of Soil Science* 106:29-34.
6. Chave, K. E., and R. F. Schmalz. 1966. Carbonate-seawater interactions. *Geochim et Cosmochim. Acta* 30:1037-1048.
7. Davies, C. W. 1962. *Ion association*. Butterworths, London. 190 p.
8. Doner, H. E., and P. F. Pratt. 1968. Solubility of calcium carbonate precipitated in montmorillonite suspensions. *Soil Science of America Proceedings* 32:743-744.
9. Doner, H. E., and P. F. Pratt. 1969. Solubility of calcium carbonate precipitated in aqueous solutions of magnesium and sulfate salts. *Soil Science Society of America Proceedings* 33:690-693.
10. Eaton, F. M. 1950. Significance of carbonates in irrigation waters. *Soil Science* 69:123-133.
11. Eldridge, E. F. 1950. *Return irrigation waters characteristics and effects*. U. S. Department of Health, Education and Welfare, Region IX, Portland, Oregon.
12. Fisher, R. B. 1962. Surface of precipitated particles. *Record of Chem. Progress* 23:93-103.

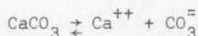
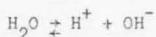
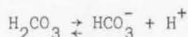
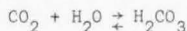
13. Garrels, R. M., and C. L. Christ. 1965. Solutions, minerals and equilibria. Harper and Row, New York. p. 93-122.
14. Greenwald, I. 1941. The dissociation of calcium and magnesium carbonates and bicarbonates. *Journal of Biological Chemistry* 141:789-796.
15. Kern, D. M. H. 1960. The hydration of carbon dioxide. *Journal of Chemistry Education* 37:14-23.
16. Langelier, W. F. 1936. The analytical control of anti-corrosion water treatment. *Journal of American Water Work Association* 28:1500-1521.
17. Leitmeir, H. 1909. Die absätze des mineralwassers rohitsch-saverbrunn steiermark. *Z. Kryst.* 47:104 (Original not seen). Cited by Bischoff, J. L. 1968. *Journal Geophysical Research* 73:3315-3322.
- ✓ 18. Nakayama, K. S. 1968. Calcium activity, complex and ion-pair in saturated CaCO_3 solution. *Soil Science* 106:429-434.
- ✓ 19. Olsen, S. R., and F. S. Watanabe. 1959. Solubility of calcium carbonate in calcareous soils. *Soil Science* 88:123-129.
20. Ponnampuruma, F. N. 1967. A theoretical study of aqueous carbonate equilibria. *Soil Science* 103:90-100.
21. Pratt, P. F., R. L. Bronson, and H. D. Chapman. 1960. Effect of crops fertilizer and leaching on carbonate precipitation and sodium accumulation in soil irrigated with water containing bicarbonate. Translated from *International Soil Science Society Congress, 7th, Madison.* 2:185-192.
22. Pytkowicz, R. M. 1965. Rates of inorganic calcium carbonate nucleation. *Science* 146:196-199.
23. Suito, E., A. Masafumi and T. Arakawa. 1955. Surface area measurement of powder by adsorption in liquid phase (I). *Bulletin Inst. Chem. Research. Kyoto University* 33:1-7.
24. Weyl, P. K. 1961. The carbonate saturometer. *Journal of Geology* 69:32-44.
25. Wilcox, L. V. 1955. Classification and use of irrigation waters. U. S. Department of Agriculture, Washington, D. C. Circular No. 969. 19 p.

APPENDIXES

Appendix A

Development of the Carbonate Saturation Theory after Weyl (24)

The carbonate saturometer is based upon the following equations and equilibrium constants:



$$K_a'_1 = \chi(\text{HCO}_3^-) / ((\text{H}_2\text{CO}_3) + (\text{CO}_2)) \quad (15)$$

$$K_a'_2 = \chi \cdot (\text{CO}_3^{--}) / (\text{HCO}_3^-) \quad (16)$$

Where $K_a'_1$ and $K_a'_2$ are apparent equilibrium constants based on concentrations, χ is the hydrogen ion activity.

The conservation of total carbonate in solution is expressed by:

$$(\text{H}_2\text{CO}_3) + (\text{CO}_2) + (\text{HCO}_3^-) + (\text{CO}_3^{--}) = y_0 + y \quad (17)$$

Where y_0 is the original (total) amount of carbonate present and y is the amount of carbonate added to the solution. Expressing equation (17) in terms of equations (15) and (16) it becomes:

$$(\text{HCO}_3^-) \cdot 1 + \left(\frac{\chi}{K_{a1}} + \frac{K_{a2}}{\chi} \right) = y_0 + y \quad (18)$$

The conservation of charge requires that electroneutrality be maintained in solution, this can be expressed as:

$$(\text{HCO}_3^-) + (\text{OH}^-) + 2(\text{CO}_3^{2-}) + \sum_{i=1}^N iY^{-i} = (\text{H}^+) + \sum_{j=1}^N jX^{+j} \quad (19)$$

Where Y^{-i} represents the total concentration of all anions of charge (-i) which do not react with the H^+ ion. X^{+j} represents the total concentrations to all cations of charge (+j) which do not react with the H^+ ion.

We now define P as the net positive charge in the original solution of those ions whose concentrations can be changed without changing the hydrogen ion concentration.

$$P = \sum_{j=1}^N jX^{+j} - \sum_{i=1}^N iY^{-i} \quad (20)$$

This allows equation (19) to be rewritten as:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) - (\text{H}^+) = P \quad (21)$$

We now define $N(\chi)$ as a function of the hydrogen ion activity.

$$N(\chi) = (\text{OH}^-) - (\text{H}^+) \quad (22)$$

Writing equation (21) in terms of $N(\chi)$ we obtain:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) + N(\chi) = P \quad (23)$$

If we now examine what happens to equation (23) when we make small additions of strong acid, base or solution HCO_3^- or $\text{CO}_3^{=}$.

For the addition of strong acid (+z), base (-z):

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) + N(\chi) = P - z \quad (24)$$

For the addition of soluble carbonate:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) + N(\chi) = P + 2y \quad (25)$$

For the addition of soluble bicarbonate:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) + N(\chi) = P = y \quad (26)$$

The next part of the development involves the combination of the conservation of charge equation and the conservation of total carbonate. Utilizing equations (15) and (16) we obtain:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) = (\text{HCO}_3^-) \left[1 + \frac{2K_{a2}}{\chi} \right] \quad (27)$$

Substituting for (HCO_3^-) from equation (18) we obtain:

$$(\text{HCO}_3^-) + 2(\text{CO}_3^{=}) = (y_0 + y) \left[\frac{1 + 2(K_{a2}/\chi)}{1 + \chi/K_{a1} + K_{a2}/\chi} \right] \quad (28)$$

We now define a function $F(x)$ such that:

$$F(x) = \frac{1 + 2K'_a{}_2/x}{1 + x/K'_a{}_1 + K'_a{}_2/x} - 1 = \frac{K'_a{}_1 K'_a{}_2 - x^2}{K'_a{}_1 x + x^2 + K'_a{}_1 K'_a{}_2} \quad (29)$$

To obtain the working equations we express the sum $(\text{HCO}_3^-) + (\text{CO}_3^{2-})$ in equations (24, 25, 26) in terms of $F(x)$.

For the addition of y' moles of carbonate:

$$y_o[1 + F(x)] + N(x) = P + y'[1 - F(x)] \quad (30)$$

For the addition of y moles of bicarbonate:

$$y_o[1 + F(x)] + N(x) = P - yF(x) \quad (31)$$

For the addition of $(+z)$ equivalents of strong acid or $(-z)$ equivalents of strong base:

$$y_o[1 + F(x)] + N(x) = P - z \quad (32)$$

It is now possible to determine $F(x)$ by a comparison of equation (31) and (32):

$$F(x) = \frac{z}{y} \text{ (acid-bicarbonate comparison)} \quad (33)$$

By determining the amount of base $(-z)$ or acid $(+z)$ necessary to produce the same change in pH (ΔpH) as a standard addition of bicarbonate produces, $F(x)$ can be calculated.

A comparison of equations (30) and (32) results in:

$$-y' = \frac{z}{1 - F(x)} \quad (34)$$

By determining the amount of base or acid necessary to produce the same change in pH (ΔpH) as results when the water is equilibrated with

a solid CaCO_3 and utilizing $F(x)$ calculated above, the number of moles (y') of CaCO_3 which dissolved or precipitated can be determined.

Appendix B

Calculation of aCa^{++} , aMg^{++} , and $aHCO_3^-$ as Effected by Ion-pair Formation

For waters containing OH^- , HCO_3^- and CO_3^{--} as the only complexing species, the total calcium (Ca_t), total magnesium (Mg_t) and total HCO_3^- (HCO_{3t}) can be expressed as follows:

$$Ca_t = [Ca^{++}] + [Ca(HCO_3)^+] + [CaCO_3^0] + [Ca(OH)^+] \quad (35)$$

and

$$Mg_t = [Mg^{++}] + [Mg(HCO_3)^+] + [MgCO_3^0] + [Mg(OH)^+] \quad (36)$$

and

$$HCO_{3t} = [HCO_3^-] + [CO_3^{--}] + [H_2CO_3] + [Ca(HCO_3)^+] + [Mg(HCO_3)^+] + [CaCO_3^0] + [MgCO_3^0] \quad (37)$$

where brackets[] represent the concentration, in moles per liter, of the various ions and ion-pairs in solution. Considering the Ca^{++} ion alone, equation (35) can be expressed in terms of activities and ionic activity coefficients:

$$Ca_t = \frac{aCa^{++}}{\gamma Ca^{++}} + \frac{aCa(HCO_3)^+}{\gamma Ca(HCO_3)^+} + \frac{aCa(OH)^+}{\gamma Ca(OH)^+} + \frac{aCaCO_3^0}{\gamma CaCO_3^0} \quad (38)$$

where a represents the activity of a particular ionic specie and γ represents its ionic activity coefficient.

Since $CaCO_3^0$ is an uncharged species the assumption is made that $\gamma CaCO_3^0$ is unity. In addition, it is assumed that both $\gamma Ca(HCO_3)^+$ and

$\gamma\text{Ca}(\text{OH})^+$ are of the same magnitude as γHCO_3^- . The above equation can now be written:

$$\text{Ca}_t = \frac{a\text{Ca}^{++}}{\gamma\text{Ca}^{++}} + \frac{a\text{Ca}(\text{HCO}_3)^+}{\gamma\text{HCO}_3^-} + \frac{a\text{Ca}(\text{OH})^+}{\gamma\text{HCO}_3^-} + a\text{CaCO}_3^0 \quad (39)$$

Considering the appropriate expressions for the dissociation constants of the ion-pairs and factoring out $a\text{Ca}^{++}$ the equation (39) becomes:

$$\text{Ca}_t = a\text{Ca}^{++} \left(\frac{1}{\text{Ca}^{++}} + \frac{a\text{HCO}_3^-}{\text{Kd}_2 \gamma\text{HCO}_3^-} + \frac{a\text{OH}^-}{\text{Kd}_3 \gamma\text{HCO}_3^-} + \frac{a\text{CO}_3^{=}}{\text{Kd}_1} \right) \quad (40)$$

where $\text{Kd}_1 = a\text{Ca}^{++} a\text{CO}_3^{=} / a\text{CaCO}_3^0$;

$$\text{Kd}_2 = a\text{Ca}^{++} a\text{HCO}_3^- / a\text{Ca}(\text{HCO}_3)^+$$

and $\text{Kd}_3 = a\text{Ca}^{++} a\text{OH}^- / a\text{Ca}(\text{OH})^+$

Introducing the first and second dissociation constants of carbonic acid and the dissociation constant of water, allows equation (40) to be written in terms of experimentally measurable quantities.

$$\text{Ca}_t = a\text{Ca}^{++} \left(\frac{1}{\gamma\text{Ca}^{++}} + \frac{\text{K Ka}_1 \text{PCO}_2}{\text{Kd}_2 a\text{H}^+ \gamma\text{HCO}_3^-} + \frac{\text{Kw}}{\text{Kd}_3 a\text{H}^+ \gamma\text{HCO}_3^-} + \frac{\text{K Ka}_1 \text{Ka}_2 \text{PCO}_2}{\text{Kd}_1 (a\text{H}^+)^2} \right) \quad (41)$$

where

$$\text{Ka}_1 = a\text{H}^+ a\text{HCO}_3^- / a\text{H}_2\text{CO}_3 = 10^{-6.38}$$

$$K_{a_2} = aH^+ aCO_3^{=} / aHCO_3^- = 10^{-10.31}$$

$$K = aH_2CO_3 / PCO_2 = 10^{-1.47}$$

rearranging and solving for aCa^{++} equation (41) becomes:

$$aCa^{++} = Ca_t / \left[\frac{1}{\gamma Ca^{++}} + \frac{KKa_1 PCO_2}{Kd_2 aH^+ \gamma HCO_3^-} + \frac{Kw}{Kd_3 aH^+ \gamma HCO_3^-} + \frac{KKa_1 Ka_2 PCO_2}{Kd_1 (aH^+)^2} \right] \quad (42)$$

expressing the above equation in terms of Ca^{++} concentration results in the following:

$$[Ca^{++}] = Ca_t / \left[1 + \frac{KKa_1 PCO_2 \gamma Ca^{++}}{Kd_2 aH^+ \gamma HCO_3^-} + \frac{Kw \gamma Ca^{++}}{Kd_3 aH^+ \gamma HCO_3^-} + \frac{KKa_1 Ka_2 PCO_2 \gamma Ca^{++}}{Kd_1 (aH^+)^2} \right] \quad (43)$$

Treating Mg^{++} ion in a similar fashion and using the same assumptions results in the following equations:

$$aMg^{++} = Mg_t / \left[\frac{1}{\gamma Mg^{++}} + \frac{KKa_1 PCO_2}{Kd_4 aH^+ \gamma HCO_3^-} + \frac{KKa_1 Ka_2 PCO_2}{Kd_5 (aH^+)^2} + \frac{Kw}{Kd_6 aH^+ \gamma HCO_3^-} \right] \quad (44)$$

and

$$[Mg^{++}] = Mg_t / \left[1 + \frac{KKa_1 PCO_2 \gamma Mg^{++}}{Kd_4 aH^+ \gamma HCO_3^-} + \frac{KKa_1 Ka_2 PCO_2 \gamma Mg^{++}}{Kd_5 (aH^+)^2} + \frac{Kw \gamma Mg^{++}}{Kd_6 aH^+ \gamma HCO_3^-} \right] \quad (45)$$

where

$$Kd_4 = aMg^{++} aHCO_3^- / aMg(HCO_3)^+$$

$$Kd_5 = aMg^{++} aCO_3^{=} / aMgCO_3^0$$

$$Kd_6 = aMg^{++} aOH^- / aMg(OH)^+$$

Applying a similar treatment to equation (37) for HCO_3^- total we obtain:

$$\begin{aligned}
 a\text{HCO}_3^- = \text{HCO}_3^- / & \left(\frac{1}{\gamma_{\text{HCO}_3^-}} + \frac{K_{a_2}}{\gamma_{\text{CO}_3^{2-}} a\text{H}^+} + \frac{a\text{H}^+}{K_{a_1}} + a\text{Ca}^{++} \left[\frac{1}{K_{d_2} \gamma_{\text{HCO}_3^-}} + \frac{K_{a_2}}{a\text{H}^+ K_{d_1}} \right] + \right. \\
 & \left. a\text{Mg}^{++} \left[\frac{1}{K_{d_5} \gamma_{\text{HCO}_3^-}} + \frac{K_{a_2}}{a\text{H}^+ K_{d_4}} \right] \right) \quad (46)
 \end{aligned}$$

The effect of ion-pair formation on $a\text{Ca}^{++}$, $a\text{Mg}^{++}$ and $a\text{HCO}_3^-$ can now be measured.

Appendix C

Computer Program

The following is the computer program for the calculation of activities of Ca^{++} , Mg^{++} , HCO_3^- and H^+ and the calculation of the amount of CaCO_3 which precipitated or dissolved.

A Input needed

1. On data cards
 - a. Total calcium (CAT(M))
 - b. Total bicarbonate (HCO3T(M))
 - c. Total magnesium (MGT(M))
 - d. Partial pressure CO_2 (PCO2)

B Output

1. Activities of H^+ , Ca^{++} , Mg^{++} , HCO_3^- before and after adjustment for ion-pair formation.
2. X2 = amount CaCO_3 precipitated or dissolved.

C Variables

1. CCA = Concentration Ca^{++}
2. ACA = Activity of Ca^{++}
3. CCO3 = Concentration of CO_3^-
4. ACA = Activity of CO_3^-
5. AHCO = Activity of HCO_3^-
6. AMG = Activity of Mg^{++}
7. EEKSP = Activity product before precipitation or solution of CaCO_3


```

DIMENSION CAT(M), HCO3T(M), MGT(M), PCO2(M)
REAL MGT
C ACTIVITY COEFFICIENTS
GC03 = .43
GCA = .43
GMG = .43
GHCO3 = .81
C EQUILIBRIUM CONSTANTS AS DEFINED IN TEXT OF
DISSERTATION
AKA1 = 1.72E-04
AKA2 = 5.60E-11
AK1 = 3.39E-02
AK2 = 2.42E-03
AKSP = 4.787E-09
AKW = 1.0E-14
AKD1 = 3.29E-05
AKD2 = 5.64E-02
AKD3 = 5.02E-02
AKD4 = 3.98E-04
AKD5 = 6.91E-02
AKD6 = 2.63E-03
DO20 N = 1,M
20 READ(5,1) CAT(M), HCO3T(M), MGT(M), PCO2(M)
1 FORMAT(4E10.2)
C CALCULATION ON INITIAL ACTIVITIES BEFORE ION-PAIR
C CORRECTION
AHC03 = HCO3T(M)*GHCO3
ACA = CAT(M)*GCA
AMG = MGT(M)*GMG
C ITERATION SEQUENCE TO CALCULATE ACA, AMG, AHC03, AH
C AS EFFECTED BY ION-PAIR FORMATION
DO 9 J = 1,10
PH = -ALOG(AKA1XAK2)+ALOG(AHC03)-ALOG(AK1*PCO2(M))
AH = EXP(-PH)
WRITE (6,4) AH, AHC03, ACA, AMG, CAT(M), HCO (M)
1MGT(M), PCO2(M)
4 FORMAT (10X, 8E12.5)
ACA = CAT(M)/(1./GCA+(AK1*AKA1*PCO2(M))/(AKD2*AH
1*6HCO3)+AKW/(AKD3*AH*GHCO3)+(AK1*AK2AKA1
2*AKA2*PCO2(M)/(AKD1*AH**2))
AMG = MGT(M)/(1.1GMG+(AK1*AK2*AKA1*PCO2(M)/(AK05
1*AH*GHCO3)+AKW/(AKD6*AH*GHCO3)+(AK1*AK2*AKA1*
2AKA2*PCO2)/(AKD4*AH**2))
A = 1./GHCO3
B = AKA2/(GC03*AH)
C = AH/(AK2*AKA1)
D = (ACA*AKA2)/(AKD1*AH)
E = ACA/(AKD2*GHCO3)
F = AMG*AKA2)/(AKD4*AH)
G = AMG/(AKD5*GHCO3)
AHC03 = HCO3T(M)/(A+B+C+D+E+F+G)
9 CONTINUE

```

```
C  CALCULATION OF AMOUNT OF CaCO3 PRECIPITATED OR
C  DISSOLVED AS EFFECTED BY ION PAIR FORMATION
   AC03 = (AKA2*AHCO3)/AH
   EEKSP = ACA*AC03
   EE = EEKSP/AKSP
   CCA = ACA/GCA
   CC03 = AC03/GC03
   IF(EE) 50, 60, 70
70  AA = EE
   BB = -EE*(CC03+CCA)
   CC = (EE-1)*(CC03*CCA)
   WRITE (7,75)
75  FORMAT (5X,'WATER UNDERSATURATED X2 = AMOUNT
   DISSOLVED',)
   GO TO 80
50  AA = EE
   BB = EE*(CC03+CCA)
   CC = (EE-1)*(CC03*CCA)
   WRITE (6,55)
55  FORMAT (5X,'WATER SUPERSATURATED X2 = AMOUNT
   PRECIPITATED',)
   GO TO 80
60  WRITE (6,65)
65  FORMAT (5X,'WATER SATURATED X2 = 0')
   GO TO 10
80  X = (-BB-SQRT(BB**2-4.*AA*CC))/(2.*AA)
   WRITE (6,85) X2
85  FORMAT (5X,'X2 = ', E12.5)
10  CONTINUE
   STOP
   END
```

VITA

John J. Hassett

Candidate for the Degree of

Doctor of Philosophy

Dissertation: Magnesium Ion Inhibition of Calcium Carbonate
Precipitation and its Relation to Water Quality

Major Field: Soil Chemistry

Biographical Information:

Personal Data: Born Spokane, Washington, September 5, 1941, son
of Raymond J. and Olive D. Hassett; married Gloria Blamires
May 31, 1963; two children--David John, Michael Raymond.

Education: Attended Dugway High School, Dugway, Utah; graduated
from Ben Lomond High School in 1959; received the Bachelor
of Science degree from Weber State College, with a major
in botany in 1964; received the Master of Science degree
from Utah State University with a major in soil chemistry
at Utah State University in 1967; completed requirements for
Doctor of Philosophy degree in soil chemistry at Utah State
University in 1970.

Professional Experience: 1964 to present, research assistant;
Utah State University 1964-1965, 1966-1968 and 1969-1970;
Fellow University Research Fellowship 1965-1966, 1968-1969.