

ABSTRACT OF THESIS

CARBON DIOXIDE EQUILIBRIA STUDIES
OF
SOILS AND CLAYS

by

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ABSTRACT

Carbon dioxide has been recognized as a common constituent of the soil system for more than a century. The carbon dioxide content of the soil air is known to vary from approximately 0.03 percent to 12 percent or more, in comparison to an average of 0.03 percent in the atmosphere above the soil.

The hydrogen-ion concentration of an aqueous system is affected by the partial pressure of CO_2 in the contacting atmosphere. Investigations of the factors influencing the hydrogen-ion concentration of soils have been extensive, yet few workers have attempted to control CO_2 pressure or determine the importance of the CO_2 variable. A confusion of data and theory exists, particularly with respect to calcareous soils. Identification of soil properties or characteristics, on the basis of hydrogen-ion concentration determinations, requires full consideration of the CO_2 variable.

The problem

The problem for which an answer is sought in this thesis is: What are the effects of some significant, variable constituents of calcareous soils on the hydrogen-ion

concentration when the soils are at equilibrium with known, constant, partial pressures of CO₂?

Problem analysis.---The following subquestions were investigated:

1. What are the effects of: type of clay mineral, sodium, calcium carbonate, sodium chloride and gypsum on the pH of clay suspensions at equilibrium with various, known, partial pressures of CO₂?
2. Are the pH values of soils at equilibrium with known, partial pressures of CO₂ useful criteria of such soil properties as: type of clay mineral, nature and relative proportions of exchangeable bases, soluble salts and permeability.

Delimitation.---The study was limited to the one-micron clay separates of bentonite, kaolin, the Fort Collins loam soil from the Colorado Agricultural Experiment Station farm, and a Grand Junction Area soil, number 57A. Twelve selected soils, including 57A, from the Grand Junction Area of Colorado were also studied.

Methods

To determine the relationship of soil pH at CO₂ equilibrium to important variables in the soil system, the problem was studied in three phases.

Preliminary studies.---Apparatus including a

large pressure tank, reducing valves and connecting lines, a constant temperature water bath and 100-milliliter wide-mouthed glass jars were assembled. The jars were partially filled with fixed amounts of soil suspensions and fitted with three-holed rubber stoppers to support a gas bubbler and two pH-meter electrodes. Mixtures of air and CO_2 were made in the tank, analyzed for CO_2 by the method of Wilson and coworkers, and bubbled through the soil suspensions. The time necessary to attain an equilibrium pH value with known, constant, partial pressures of CO_2 in the gas mixtures was determined, all pH determinations being made by use of a Beckman pH meter (Model G, glass electrode).

Equilibria studies of clay systems.—Groups of four separate clay materials less than one micron diameter were fractionated from raw bentonite, washed kaolin, the Fort Collins loam soil and a Grand Junction Area soil (57A). Supercentrifugation, sedimentation and flocculation techniques were employed. From each stock clay, six clay systems of varying sodium-calcium status were prepared by washing portions of the clays with one-normal chloride solutions of sodium and calcium, which were mixed in different ratios. sp. ?

The clays, in groups of six, were next prepared in two-percent aqueous suspensions, analyzed, and equilibrated with four known, constant, partial pressures of CO_2 . Equilibrium pH values were obtained. The procedure was

repeated three more times as calcium carbonate, sodium chloride and gypsum were added in succession to form increasingly complex systems. The pH values of 96 separate clay systems were thus obtained. The data was analyzed statistically to determine the effects of type of clay, sodium, calcium carbonate, sodium chloride and gypsum on pH at CO_2 equilibrium. The slope of the pH curves was also calculated and subjected to statistical studies for significant differences.

Equilibria studies of soils.--Suspensions of twelve Grand Junction Area soils were equilibrated at four CO_2 pressure levels. The pH values were obtained at 0.0003 atmospheres partial pressure of CO_2 for comparison with the clay-system data. Additional, rapid, approximate analyses for texture, soluble salt concentration, soluble and exchangeable sodium, calcium carbonate and gypsum were made. Samples of the soils were subjected to permeability and leaching studies. The pH of suspensions of the leached samples was determined and compared with the pH data of the unleached soils.

Results

The equilibrium pH values obtained in the 96 clay systems and 12 soils at each of four partial pressures of CO_2 were plotted against the logarithm of the corresponding partial pressure of CO_2 used. A summary of the pH curves

is presented in Figures 4, 5 and 6. The pH curves of a "check" system of Baker's C. P. calcium carbonate have been plotted with the clay systems. Grouped pH curves of the 12 Grand Junction Area soils before and after leaching are presented in Figure 12. The soils varied in texture from sandy loam to clay, contained from 0.1 percent to 3 percent or more soluble salts, varied in exchangeable sodium percentage from 2 to 80 or more, contained from 7 to 21 percent calcium carbonate, and varied in gypsum content from 0.05 to 12 milliequivalents per 100 grams of soil. The range in maximum permeability was from 0 to about 0.6 centimeters per hour, the most slowly permeable soils being 13A, 16A and 45C.

Discussion

The kaolin clays were significantly lower in mean pH than the three other clay groups, averaging 8.09 ± 0.04 at 0.0003 atmospheres partial pressure of CO_2 , in contrast to 8.37 ± 0.04 for the bentonite clays, 8.46 ± 0.06 for the Fort Collins clays, and 8.28 ± 0.06 for the Grand Junction soil 57A clays. Differences due to clay minerals did not exceed 0.5 pH unit, and were generally considerably less. The mean slopes of the pH curves of the bentonite and Fort Collins clay groups were closely related, being 0.800 ± 0.016 and 0.798 ± 0.015 respectively. The slopes of the pH curves of the 57A clay systems averaged 0.743 ± 0.010 ;

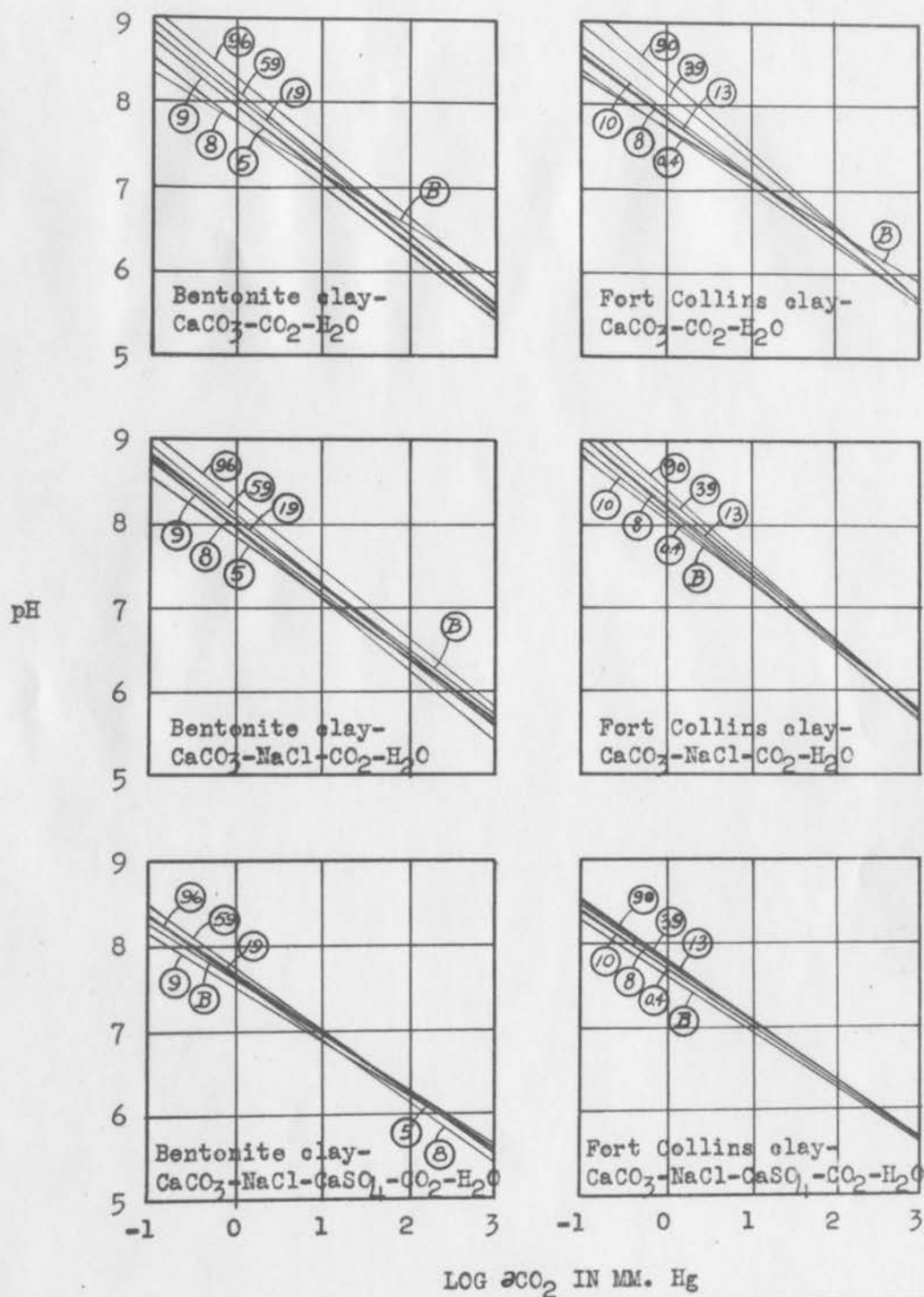


Fig. 4.--The pH curves of bentonite and Fort Collins clay systems at 20°C.
[Percent sodium of sum of cations indicated.
Baker's C.P. $CaCO_3$ systems labeled B]

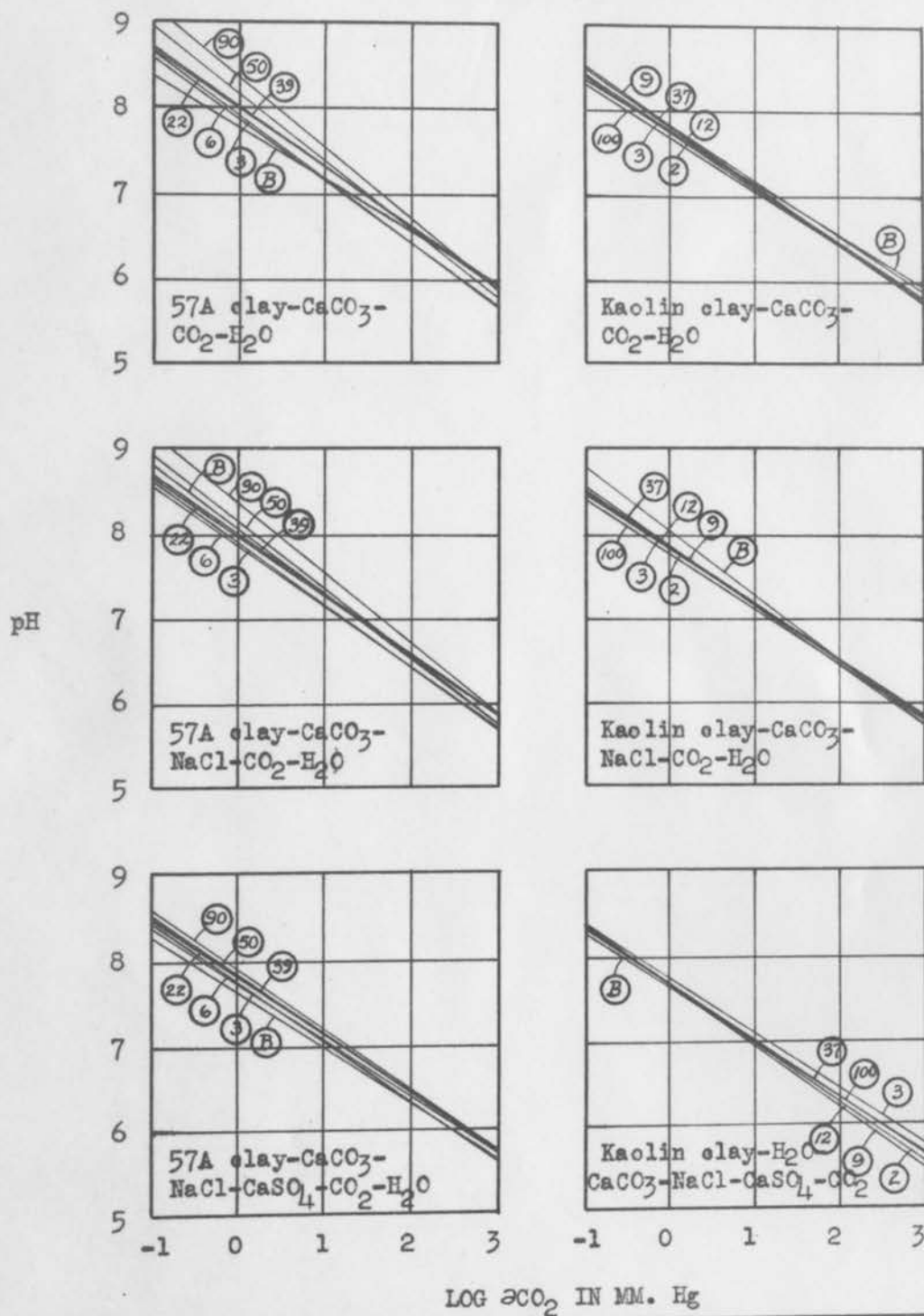


Fig. 5.--The pH curves of 57A and kaolin clay systems at 20°C.

[Percent sodium of sum of cations indicated.
Baker's C.P. CaCO₃ systems labeled B]

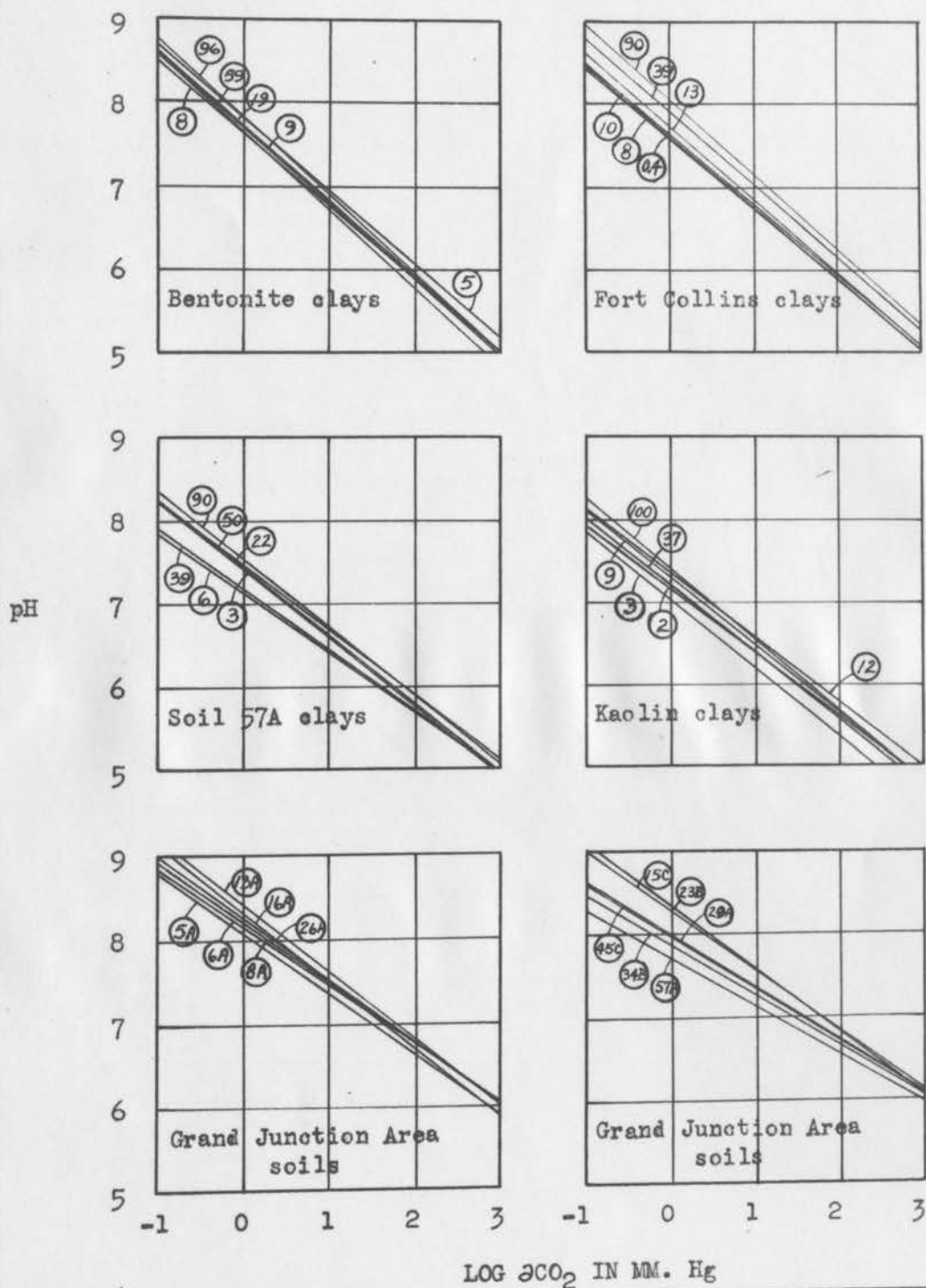


Fig. 6.--The pH curves of clays and soils at 20°C.

[Percent sodium of sum of cations indicated for the clay systems. Soil sample numbers indicated]

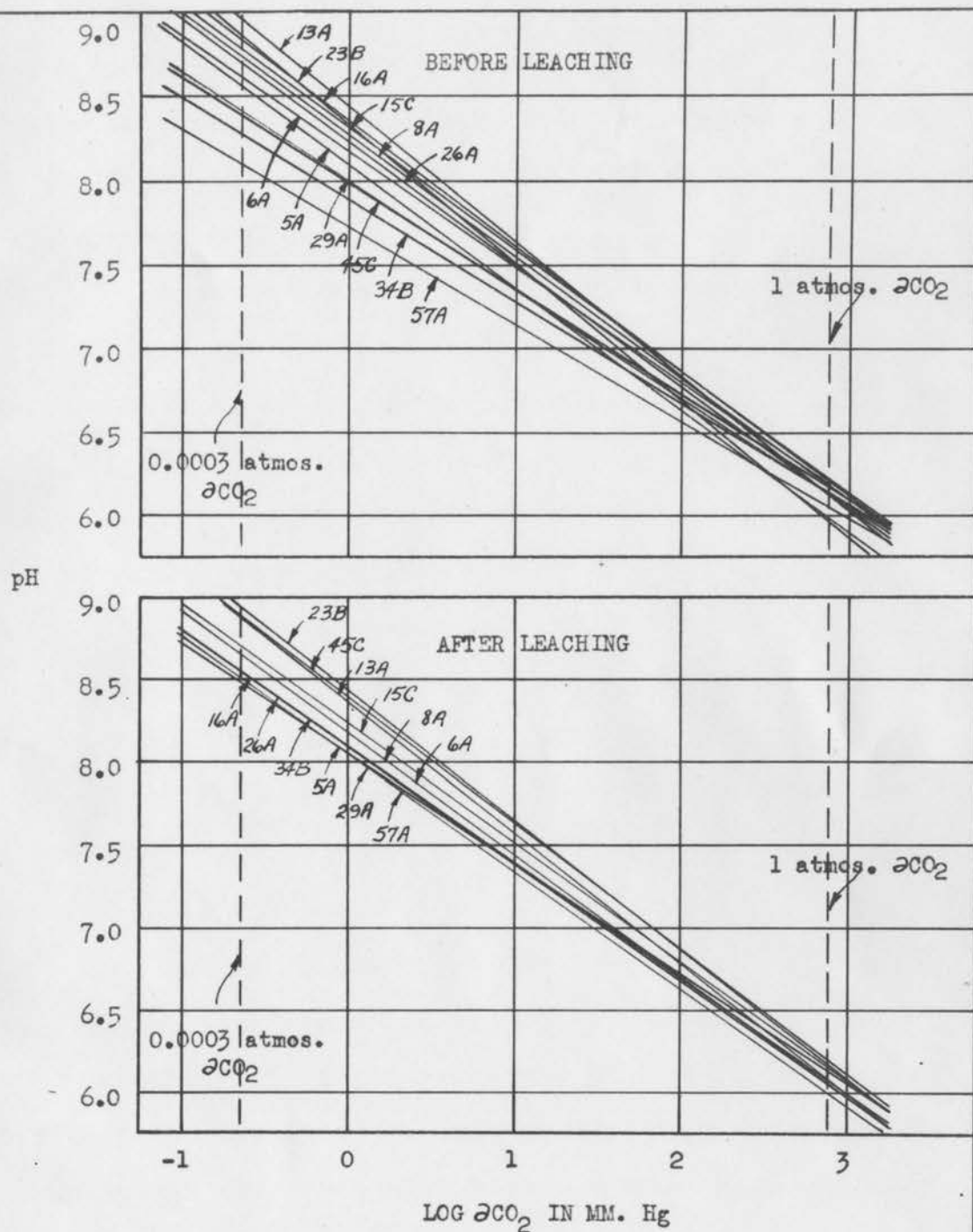


Fig. 12.--Grouped pH curves of twelve Grand Junction Area soils at 20°C.

[The soil to water ratio was 1 to 5. The soil sample number is indicated]

those of the kaolin group averaged 0.714 ± 0.013 . These values were significantly less than the mean slope values of the other two clays, but not significantly different from each other.

A trend toward higher pH at low partial pressure of CO_2 was noted with increasing sodium in all clay systems except those of kaolin or any system containing gypsum in excess. Significant direct correlations between milliequivalents of sodium per 100 grams of clay and slopes of the pH curves were obtained with similar exceptions.

Calcium carbonate had one outstanding effect in all clay systems: the pH at low CO_2 partial pressure was increased by its addition. Also, the slopes of the pH curves were slightly decreased, but remained above the 0.602 value for the slope of the pH curve of the pure $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system.

Sodium chloride, at the concentration used, had no noticeable effect on pH in the bentonite and soil 57A clay systems, but did increase the pH in kaolin and Fort Collins clay systems. The slopes of the pH curves were increased in the Fort Collins clay systems, but not in the other clay systems.

The addition of an excess of gypsum produced a marked reduction of about 0.5 pH unit in all systems at 0.0003 atmospheres partial pressure of CO_2 . Likewise, the slopes of the pH curves were significantly decreased by gypsum, except in the kaolin clay systems.

The twelve Grand Junction Area soils varied widely in texture, sodium, gypsum and soluble salt status, but all contained an excess of calcium carbonate. The equilibrium pH values of the soils varied from 8.09 to 8.95 at 0.0003 atmospheres partial pressure of CO_2 . The effects of leaching were not uniform, and the range in pH values of the leached samples was 8.48 to 8.93. Some soils increased in pH due to leaching; others decreased. The slope values of the pH curves varied from 0.582 to 0.838. The mean pH of all the soil systems was 8.62 ± 0.04 , and the mean slope of the pH curves was 0.715 ± 0.012 . All of the soils represented clay- CaCO_3 - CO_2 - H_2O systems in general pH characteristics, both before and after leaching. Modifications and differences seemed to be due largely to the variability between the samples with respect to the amounts of soluble salts, gypsum and sodium present.

The technique of determining the pH of soils at equilibrium with known, constant, partial pressures of CO_2 provided a different concept of the soils than would generally be obtained by the usual methods of pH determination. It was observed that the pH of the Grand Junction Area soils under field conditions might normally range between 7.75 and 6.5, in spite of the fact that some of the soils contained considerable sodium. The pH values of the soils at known CO_2 equilibrium were not sufficiently different in this study to provide useful criteria of such soil properties as: type of clay mineral, nature and relative proportions of exchangeable bases, soluble salts and

permeability. However, the information in conjunction with rapid, approximate analyses for significant soil constituents provided a distinct aid for the diagnosis of soil properties and capabilities for plant growth.

The need for a considerable amount of data, particularly on soil systems, with respect to equilibrium pH values, slopes of pH curves and statistics based on the results is indicated. Studies of such additional clays as illite are desirable. The need for soil atmosphere studies and CO₂ fluctuations in soils in situ is great. A more significant method of studying such CO₂ fluctuations than present techniques might be developed by the determination of pH in the field and interpolation of CO₂ pressures from previously prepared pH curves of the soils. Other soil problems, such as that of phosphate, should be examined in full consideration of CO₂ equilibria.

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T H E S I S

CARBON DIOXIDE EQUILIBRIA STUDIES

OF

SOILS AND CLAYS

Submitted by

Bruce Franklin Beacher

In partial fulfillment of the requirements

for the Degree of Master of Science

Colorado

Agricultural and Mechanical College

Fort Collins, Colorado

August, 1949

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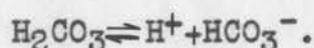
Chapter I

INTRODUCTION

Carbon dioxide has been recognized as a common constituent of the soil system for more than a century. Quantitative studies with respect to the amounts present and the influence of atmospheric, biological, chemical and physical factors thereon have been relatively extensive. The carbon dioxide content of the soil air is known to vary from approximately 0.03 percent to 12 percent or more, in comparison to an average of 0.03 percent in the atmosphere above the soil. The wide variations in the concentration of carbon dioxide commonly encountered have been linked with the heterogeneity of physical, biological and ecological influences within the soil.

The role of carbon dioxide in chemical reactions which occur in the soil system has been studied qualitatively. The extent of quantitative studies of this type is much less than justified.

Carbon dioxide dissolves in water in proportion to its partial pressure. It combines in part to form carbonic acid, which ionizes according to the equation:



The further ionization of HCO_3^- into H^+ and $\text{CO}_3^{=}$ is

exceedingly small. It is apparent, therefore, that the hydrogen-ion concentration of an aqueous system is affected by the partial pressure of CO_2 in the contacting atmosphere. The hydrogen-ion concentration of the soil solution could be expected to vary from place to place as a result of variations in the CO_2 pressure of the soil atmosphere. Plant root respiration, microbial activity, moisture fluctuations, seasonal changes and the diffusion of gases through the soil are important factors known to affect the amounts of CO_2 within the soil system.

Need for this study

Investigations of the factors influencing the hydrogen-ion concentration of soils have been extensive, yet few workers have attempted to control CO_2 pressure or measure the importance of the CO_2 variable. The use of hydrogen-ion concentration as a criterion of the nature and relative proportions of exchangeable bases, soluble constituents and various other soil properties has held major interest among soil scientists and technicians for many years. Unfortunately, a confusion of data and theory exists, particularly with respect to calcareous soils. This is due in large part to neglect of the control of CO_2 pressure in basic studies. The partial pressure of CO_2 in contact with the soil system must be known and

controlled in soil reaction studies. Identification of soil properties or characteristics, on the basis of hydrogen-ion concentration determinations, requires full consideration of the CO_2 variable. An urgent need for fundamental studies of this type exists.

The problem

The problem for which an answer is sought in this thesis is: What are the effects of some significant, variable constituents of calcareous soils on the hydrogen-ion concentration when the soils are at equilibrium with known, constant, partial pressures of CO_2 ?

Problem analysis.---The following sub-questions were investigated:

1. What are the effects of: type of clay mineral, sodium, calcium carbonate, sodium chloride and gypsum on the pH of clay suspensions at equilibrium with various, known partial pressures of CO_2 ?
2. Are the pH values of soils at equilibrium with known, partial pressures of CO_2 useful criteria of such soil properties as: type of clay mineral, nature and relative proportions of exchangeable bases, soluble salts and permeability.

Delimitation.--The study was limited to the one-micron clay separates of bentonite, kaolin, the Fort Collins loam soil from the Colorado Agricultural Experiment Station farm, and a Grand Junction Area soil, number 57A. Twelve selected soils, including 57A, from the Grand Junction Area of Colorado were also studied.

Definition of terms.--pH is the logarithm of the reciprocal of the hydrogen-ion concentration.

∂CO_2 is the partial pressure of carbon dioxide, measured in millimeters of mercury or atmospheres.

Log ∂CO_2 is the logarithm of the partial pressure of carbon dioxide measured in millimeters of mercury.

Equilibrium as herein applied is a state of balanced activities of the constituents of an aqueous system for a given set of conditions.

Equilibrium pH is the logarithm of the reciprocal of the hydrogen-ion concentration of an aqueous system at equilibrium with a known, constant, partial pressure of CO_2 .

pH curve is a graphical representation of the pH of a system at constant temperature as a function of the logarithm of the partial pressure of CO_2 .

Slope of the pH curve is the tangent of the angle the pH curve makes with the horizontal axis, and is expressed by the relationship: $\Delta\text{pH}/\Delta\log \partial\text{CO}_2$.

Chapter II

REVIEW OF LITERATURE

Soil is fundamentally a ternary system of solid, liquid and gas. The complexity of the system varies with the geographical location, parent materials and concomitant pedogenic processes which have operated to produce any one soil. In the semiarid and arid regions of the United States, the solid phase may include mineral and organic materials in various stages of weathering, calcium carbonate, gypsum and a variety of soluble salts. The soil solution, as a result, contains many ions. The cations calcium, sodium and magnesium, and the anions chloride, sulfate and bicarbonate generally predominate. Considering the additional solution of carbon dioxide from the gaseous phase, the soil solution can be very complex.

Since the partial pressure of CO_2 is not constant, the system soil- CO_2 - H_2O is dynamic. An infinite number of equilibria or near-equilibria may occur. An infinite number of pH values, each a criterion for any one equilibrium, would correspondingly occur. Some expression of this range of equilibria and pH values is desirable to obtain a concept of the soil system under

natural field conditions.

The research studies in which the CO_2 -equilibria-pH concept has been investigated are included in two broad groups: first, equilibria studies of chemical systems; and, second, carbon dioxide studies of soil systems.

Equilibria studies of chemical systems

In 1932 Byck (14) calculated pH values for pure water in equilibrium with varying partial pressures of CO_2 . By plotting pH against $\log \partial\text{CO}_2$, he graphically illustrated a fundamental, equilibria concept for the simple system $\text{CO}_2\text{-H}_2\text{O}$. The relationship between pH and $\log \partial\text{CO}_2$ was linear and reciprocal in the range of CO_2 pressure from one atmosphere to 10^{-6} atmospheres. The pH curve had a negative slope of approximately 0.5. Pure water in equilibrium with one atmosphere of CO_2 pressure had a pH of 3.95; at 0.0003 atmospheres, the pH was 5.72. These values were in agreement with those of Wiegner given by Small (55:148) in 1946.

When the system is changed to $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ by the addition of calcium carbonate, readjustments in equilibria are effected and the pH values altered. In 1929 Frear and Johnston (20) conducted determinations of the solubility of CaCO_3 (calcite) at $25^\circ\text{Centigrade}$ in water at known, constant ∂CO_2 . As the partial pressure of CO_2 is increased, the solubility of calcite increases from a

minimum of 0.52 millimoles per kilogram of water at 0.0003 atmospheres ∂CO_2 to 9.02 millimoles per kilogram at one atmosphere ∂CO_2 . A graphical plot of the bicarbonate ion concentration against the cube root of the CO_2 pressure in atmospheres was presented to ascertain the solubility of calcite at any partial pressure of CO_2 . The curve was nearly linear.

Simmons (54) provided additional data in 1939 by observing pH values in the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system at 30°C . At 0.0004 atmospheres ∂CO_2 the equilibrium pH was 8.36. At 0.0446 atmospheres ∂CO_2 the pH of the system was 6.91. The slope of the pH curve is about 0.7. Simmons observed that the increase in CO_2 pressure increased the relative concentration of hydrogen-ions much more than it did the calcium-ion concentration. This increase in H-ion concentration, coupled with its much greater specific absorability, accounted for a decrease in Ca-ion absorption measured as the CO_2 pressure was increased.

A second ternary system, $\text{NaHCO}_3\text{-CO}_2\text{-H}_2\text{O}$, has been studied by several chemists for industrial and physiological applications. In 1917, McClendon (31) determined the pH of sodium bicarbonate solutions of varying normalities at equilibrium with different, known CO_2 pressures. The pH curves of the solutions were parallel, had a negative slope of about 0.8, and were spaced about 0.85 pH unit apart vertically for each tenth difference in normal-

ity. The pH of 0.001 N NaHCO_3 at equilibrium with 0.0003 atmospheres partial pressure of CO_2 and 20°C . was about 7.95. The pH varied directly with temperature if the CO_2 tension was held constant, the variation being 0.01 pH unit for each degree Centigrade. Finding parallelism of these pH curves with those of blood and sea water, McClendon concluded that all biological media, excluding those exceptionally rich in phosphates, have the same slope of pH curve. A moderate dilution of sea water with distilled water did not appreciably change the pH, if the CO_2 tension was near that of the atmosphere and the solution was not agitated with nor exposed to the air. McClendon further reported that neutral salts slightly decreased the hydrolysis of bicarbonate and decreased pH. The report was preliminary and great accuracy was not claimed for the data.

Hastings and Sendroy (23) in 1925 and Stadie and Hawes (57) in 1931 developed equations relating to equilibria in the system $\text{NaHCO}_3\text{-CO}_2\text{-H}_2\text{O}$. In 1932 Wilson, Orcutt and Peterson (64) applied these concepts of equilibria in a sodium system to a method for the determination of CO_2 in gas mixtures. In a discussion of the equilibria relations, the authors stated:

.....In an aqueous solution of carbonic acid and sodium bicarbonate pH will be a function of the activities of the bicarbonate ion and carbonic acid present.....The latter depends on the

partial pressure of carbon dioxide....in equilibrium with the solution. If the activity of the bicarbonate ion is fixed, then the pH is a function solely of the partial pressure of the carbon dioxide that is in equilibrium with the sodium bicarbonate solution....carbonic acid is only very slightly ionized....the effective concentration (or activity) of the bicarbonate ion is sensibly that of the sodium bicarbonate present in the solution (65:357).

Wilson and coworkers bubbled air mixtures of known, constant CO_2 content through 0.001 and 0.0107 N solutions of sodium bicarbonate, and determined the pH at equilibrium. By plotting the pH data against log millimeters partial pressure of CO_2 , they constructed a calibration curve. Then, by bubbling gas of unknown CO_2 composition through the sodium bicarbonate solutions, the authors were able to determine the partial pressure of CO_2 by reference to the curve. The method was useful with a fair degree of accuracy for gas mixtures containing from 0.03 to 7 percent CO_2 .

Equilibria relations in aqueous systems become increasingly complex as additional soluble or partly soluble constituents are included. In 1923 Shipley and McHaffie (52) conducted hydrogen-ion determinations in water solutions of CO_2 , CaSO_4 and CaCO_3 . When CO_2 was bubbled through conductivity water, the pH showed a sudden drop and then gradually leveled off near the saturation point for CO_2 . After twenty minutes, constant readings of pH 3.96 were obtained. Almost identical

readings were noted in saturated CaSO_4 solutions. Water in contact with CaCO_3 in the absence of CaSO_4 and CO_2 will be basic, they concluded, and will have a pH of 9.38. If CaSO_4 is present, the H-ion concentration will be increased and approach the neutral point. Ground waters saturated with CO_2 at a partial pressure of one atmosphere and in contact with soil containing CaCO_3 and CaSO_4 will be acidic (pH 5.11). In noncalcareous soils the solutions will be more acidic, having a pH of 4.0. The effect of gypsum was to increase the H-ion concentration when the soil contained calcareous material.

The calcite solubility work of Frear and Johnston in 1929 (20), previously cited, contributed additional data of value in the interpretation of equilibria in complex systems. The solubility of calcite was found to be slightly decreased in solutions saturated with gypsum at all levels of CO_2 pressure in the range 0.0003 to one atmospheres of pressure. In contrast, the solubility of calcite was practically doubled in the presence of one molal sodium chloride, and increased markedly with increasing chloride concentration at nearly constant CO_2 pressure. A portion of the data of Frear and Johnston is presented in Table 1.

The application of these fundamental experiments to more complex systems, e.g. clay- or colloid-bases- CO_2 - H_2O has been very limited, and the influence of clay or

Table 1.--THE SOLUBILITY OF CALCITE IN AQUEOUS SYSTEMS AT
25°C_a

∂CO_2 atmos.	System		∂CO_2 atmos.	System	
	H ₂ O	H ₂ O-CaSO ₄		H ₂ O-NaCl	
	HCO ₃ conc.mml./kilo.			Cl conc. mml./kilo.	HCO ₃ conc. mml./kilo.
0.125	4.21	3.16	0.965	3.79	8.96
0.216	5.13	3.97	0.965	14.80	9.37
0.343	6.08	4.80	0.965	34.80	9.67
0.528	7.06	5.76	0.963	297.00	12.34
0.729	8.04	6.72	0.968	816.00	14.67
1.000	9.02	7.70	0.968	1154.00	16.18

^aTable summarizes portion of data, Frear and Johnston(20)

colloid in the systems has not been adequately studied. Findlay (17, 18) noted in 1908 and 1913 that the solubility of carbon dioxide in water varies with the type of colloid present. In solutions of Fe(OH)₃ and gelatin, the solubility is greater than in water. In those of dextrin, starch and glycogen it is less. In arsenious sulphide, silicic acid and albumen it is approximately the same as in water. In the 1939 study previously cited, Simmons (54) observed the pH values of clay-CaCO₃-H₂O systems to be higher than the pH values of corresponding CaCO₃-H₂O systems, and that the CO₂ partial pressure does affect the absorption of calcium by a hydrogen clay. The amounts of calcium absorbed decreased as the CO₂ pressure was increased. At the lower pressures, the change in Ca ab-

sorption is a linear function of the cube root of the CO_2 pressure when expressed in atmospheres. A plot of Simmons' observed pH values of the clay- $\text{CaCO}_3\text{-H}_2\text{O}$ system against the log ∂CO_2 again provides the typical straight-line relationship, the slope of the curve being approximately 0.63. The curve is somewhat higher on the pH scale than that of the pure calcite aqueous system.

Carbon dioxide studies of soil systems

The fundamental work of identifying carbon dioxide in the soil, and methods of determination of CO_2 were initiated during the latter part of the 19th Century. Russell and Appleyard (50) in 1915 and Turpin (61) in 1920 adequately summarized the pioneering work of Bous-singault and Lewy, Pettenkofer, Ebermayer, Demoussy, Lau and many others in connection with their own extensive studies of CO_2 in the soil atmosphere. The more recent studies of Boynton and Reuther (9) in 1941, Furr and Aldrich (21) and Neller (38) in 1943, and Reuther and Crawford (49) in 1947 have contributed more significant and reliable data of CO_2 variations in the soil atmosphere. On the basis of the existing studies, the CO_2 concentration of the soil atmosphere ranges from 0.03 to 12 percent or more.

Stocklasa (59) in 1906 and Stocklasa and Ernest (60) in 1907 noted and measured the importance of plant

roots and organisms in contributing CO_2 to the soil mass, calling particular attention to the fine roots and root hairs of sugar beets. They concluded that the carbonic acid formed as a result of respiration exerts a direct solvent action on the phosphates of the soil. Similar studies of this type have been conducted to the present time (7, 12, 24, 35, 36, 37, 39, 40, 41, 42, 43).

Hoagland and Sharp (25) conducted in 1918 what appears to have been the initial study of equilibria in soil- CO_2 - H_2O systems. Soil suspensions were equilibrated with mixtures of hydrogen and pure CO_2 gases in varying proportions. Voltmeter readings were taken until values checked within 0.005 volts. The results are summarized as follows:

1. The pH of acid soils was not markedly affected by CO_2 comprising less than 10% of a gas mixture.
2. The H-ion concentration of slightly alkaline soils was slightly increased by the treatments.
3. A notable increase in H-ion concentration occurred in soils containing the alkali carbonates.
4. None of the CO_2 treatments produced an alkaline reaction.
5. No permanent change in soil reaction occurred due to CO_2 .

During the same year Noyes and Yoder (40) presented the results of experiments in the greenhouse concerning the nature and causes of soil acidity. Pepper plants were grown in pots containing soils variously treated with lime and fertilizer materials, and through which CO_2 was passed at different rates. They found that soil kept at

one-half its waterholding capacity increased in acidity, the increase being modified by the various fertility treatments.

A relationship between pH values and CO_2 in soils was noted by Atkins (2) in 1922. Theoretical maximum alkalinities of 9.01 for CaCO_3 , pH 10 for MgCO_3 and pH 10 or higher for Na_2CO_3 in aqueous systems were obtained experimentally in the absence of CO_2 . The pH of $\text{Ca}(\text{HCO}_3)_2$ in equilibrium with the gases of the atmosphere was given as 8.37 at 16°C ., increasing with temperature increments. A high CO_2 content in the soil was given as the reason for lower pH values than those observed in the absence of CO_2 . Production of carbon dioxide by bacteria caused a decrease in soil alkalinity from 8.7 to 7.2 or less, the rate being more rapid in the upper six inches of the profile than below.

In 1923 Kelley and Thomas (28) shook 200-gram samples of sodium soils for one hour with one-liter portions of water previously partially saturated with CO_2 . As the amount of CO_2 in the water was increased:

1. Soluble CO_3 decreased.
2. Concentration of HCO_3 increased.
3. The pH decreased.
4. The solubility of calcium increased, the increase being roughly proportional to the CaCO_3 content of the soils.

The beneficial effect of manure in black alkali soils was believed due in part to CO_2 formed in decomposition.

Pure water at equilibrium with CaCO_3 was reduced in reaction from a pH above 8.5 to one well on the acid side of neutrality by merely passing CO_2 through the suspension. It was stressed that the soil solution around the roots of plants growing in calcareous soil in either humid or arid climates is not necessarily alkaline.

Bobko and Druzhinin (7) in 1925, while determining the influence of various factors on the reaction of the soil solution, stressed that the H-ion concentration of soil extracts is regulated by a buffer system of carbon dioxide and carbonic acid. Carbon dioxide in distilled water had no influence on the pH value of unlimed soils but increased the H-ion concentration of limed soils slightly. Free CO_2 in the water extracts from a series of unlimed podsol soils and peats had practically no influence on the H-ion concentration of these extracts. In limed soils, separation of CO_2 resulted in important increases in pH. During the same year, Pierre (44) found that carbon dioxide increased the H-ion concentration of acid as well as alkaline soils, but suggested any pronounced effect would occur at the root-hair-soil solution contact rather than in the soil itself as a result of the buffer capacity of soils.

Billman and Jensen (6) in 1927 compared the use of boiled water, aerated water containing one milligram CO_2 per liter, and water containing 17.2 milligrams

of CO_2 per liter for preparing soil suspensions. For alkaline and neutral soils they found that CO_2 reduced pH; one milligram of CO_2 per liter caused no difference in pH. For the acid soils there was no effect even from the distilled water containing 17.2 milligrams of CO_2 per liter.

Small (55) presented data gathered by Kappen in 1929 on the variation in pH of percolates from different soil types at equilibrium with varying concentrations of CO_2 . The percolates were buffered only slightly against changes of pH due to carbon dioxide. The data follows:

Table 2.--THE pH OF PERCOLATES FROM DIFFERENT SOILS AT EQUILIBRIUM WITH VARYING CONCENTRATIONS OF CARBON DIOXIDE_b

Soil Type	No CO_2	1% CO_2	10% CO_2	100% CO_2
Loam-----	6.99	6.81	6.48	6.01
Sandy loam-----	6.53	6.46	6.18	5.64
Sand with humus---	6.23	5.76	5.44	5.10
Loamy sand-----	6.03	6.01	5.88	5.45
Loam-----	5.24	5.00	4.68	4.26
Sand with humus---	4.65	4.62	4.52	4.38

_bPortion of table from Small (55:149)

In 1931 McGeorge and Breazeale (36) noted the role of CO_2 in soil reaction-phosphate availability relationships, and emphasized that CO_2 is the most important single factor in the fertility of alkaline soils.

In 1935 McGeorge (34) stressed the dynamic

character of the alkali-soil system, and the nonexistence of stable equilibrium:

....determination of the pH value of alkali soils demands careful technique....most important of all, carbon dioxide....must be eliminated from the system....the maximum pH of a soil can be obtained only by the employment of carbon dioxide-free distilled water....this high pH may not be possible under field conditions....it represents the total amount of hydroxyl ions which must be neutralized by carbon dioxide exudation before normal ion absorption of roots can function.
(34:260-61)

McGeorge observed the marked effect which a small amount of CO_2 has upon the pH of alkali soils, and the modifying influence of buffers. Stating that carbon dioxide more completely influences the soil reaction of alkali soils than any other single factor, he performed a group of experiments with carbonated solutions, CO_2 -free air and unaltered air to show these effects in alkaline-calcareous soils of Arizona and an upland acid soil. A portion of the data follows:

Table 3.--SHOWING EFFECT OF AERATION WITH AIR AND CO_2 -FREE AIR ON pH VALUE OF SOIL SUSPENSIONS_c

Soil No.	Original pH	pH 3 hrs.	pH 8 hrs.	pH 24 hrs.	ppm.sol.salt in 1:5 ext.
CARBON DIOXIDE-FREE AIR					
2	8.50	8.45	8.65	8.40	140
4	10.22	10.15	10.28	9.82	4696
5	6.10	6.20	6.80	7.10	51
AIR					
2	8.50	8.15	8.25	7.85	140
4	10.20	9.80	9.74	8.90	4696
5	6.10	6.50	7.05	7.10	51

cTable a portion of McGeorge data (34:254, Table 8).

It was evident that carbon dioxide reduced the pH of the alkaline-calcareous soils but increased the pH of the acid soil "probably due to loss of carbon dioxide from the suspension". Additional data were presented to show that for every soil there is apparently an equilibrium point with relation to air. Minimum pH values, in comparison to those obtained in CO₂-free distilled water, were determined in NaCl-CaCl₂-soil systems. The pH was increasingly depressed by the more concentrated salt solutions, and by increasing amounts of the salt solutions, or by narrowing the dilution ratio of solution to soil.

Smith and others (56) reported on CO₂ effects in 1937 on the pH of the Carrington loam and Carrington and Tama silt loams of Iowa, using CO₂-saturated water or passing CO₂ through pots of the soils. The untreated Carrington loam increased in pH under the CO₂ treatment. The Carrington silt loam treated with rock phosphate showed no effects, as did the Tama silt loam. The authors concluded that CO₂ may have different effects in different soils.

Puri and Uppal (46) in 1938, using 25 soils, prepared suspensions having soil to water ratios of 1 to 10, and passed CO₂ through them. They noted that pH, determined by use of the glass electrode, decreased and soluble salts in the solutions increased, the extent of change varying with the soil type. The significance

of a ratio of approximately 0.7 between the pH values before and after CO_2 treatment was stressed. To determine the role of CO_2 in the reclamation of alkali soils, they then neutralized hydrogen-ion saturated soils with varying mixtures of calcium and sodium hydroxides. The resulting "degree of alkalinity" of the soils was expressed in terms of the percent sodium. The suspensions were equilibrated with air- CO_2 mixtures, and pH was determined. A portion of the results are summarized in the following table:

Table 4.--THE pH OF SOIL SUSPENSIONS OF VARYING ALKALINITY AT EQUILIBRIUM WITH CO_2 .^a
[The soil to water ratio was 1 to 10]

Sum of Na+Ca in milliequ- ivalents	Degree of Alkalinity	Initial pH	pH with 1% CO_2	pH with 100% CO_2
18	0	6.0	6.38	5.02
16	20	6.2	5.55	5.40
16	40	6.4	6.2	5.4
16	60	6.4	5.7	5.5
16	80	6.6	5.36	4.58
16	100	7.33	5.06	4.62

^aTable is a portion of data by Puri and Uppal (46:470)

As a result of these studies, Puri and Uppal concluded:

1. A substantial decrease in pH values occurred at all degrees of alkalinity.
2. Flocculation occurred at low pH values at all degrees of alkalinity, but not at high pH when the percent Na (of Na plus Ca) exceeded 60 to 80.
3. In the presence of CaCO_3 much sodium was brought into solution and could be leached to reduce the degree of alkalization.

A related study of salt effect and soil-water ratio on soil pH by Puri and Asghar (45) in 1938 was significant, although CO_2 equilibrium was not stressed. In the absence of salts, the same pH was obtained whether the soil to water ratio was 1 to 5 or 1 to 25. Salts lowered the pH of soils. The pH values of leached soils were higher than those of the unleached. It was noted that CaCO_3 modified soil reaction, even in the presence of normal KCl, which exhibited a greater effect in lowering the pH of the leached than of the original soil.

In a thorough discussion of soil reaction, McGeorge (33) summarized the effects of calcium carbonate and sodium in 1938. He found, in all cases, that there is a straight-line relation between the pH (determined with the glass electrode in a 1 to 10 dilution) and replaceable sodium, provided more than 10 milliequivalents of the base are involved and more than 20 percent of the exchange capacity is satisfied by sodium. In soils with an exchange capacity below 10 milliequivalents, he was unable to identify any single dominating factor. There was no apparent relation between the soluble salts (white alkali) and the pH values. A sodium-saturated clay will exhibit a higher pH when calcium carbonate is present than when it is absent. A study of the pH of soils saturated with calcium and hydrogen did not disclose any relation between the pH and the exchange capacity, or

between pH and milliequivalent amounts of Ca- and H-ions present in the clay complex.

In 1941 Bradfield (10) stated that the range of pressures of CO₂ with which we are ordinarily concerned in soils is from 0.0003 to 0.1 atmosphere, and that practically all of the calcium in solution under soil conditions is in the form of the bicarbonate. Experimentally Bradfield and Allison (11) had previously found that a suspension of calcium hydroxide and clay responded very quickly to changes in carbon dioxide pressure. Referring to the case of calcareous soils, Bradfield suggested that the many observed differences in pH were functions of carbon dioxide equilibria, and that pH values would have become approximately the same, ordinarily between 8.2 and 8.4, if all samples had been brought into equilibrium with the CO₂ of the atmosphere. Considerable time, often several (4 to 8) hours of aeration, would be necessary to reach equilibrium especially when there is only a slight excess of calcium bicarbonate present. Initial increments of gypsum lowered the pH value of an acid soil about one-half a unit. Further increments had but little effect. A similar but less pronounced phenomenon occurred in calcareous clay. It was concluded that a knowledge of the chemistry of the system soil-CaCO₃-CO₂-H₂O was basic to the entire field of soil chemistry.

Furr and Aldrich (21) studied oxygen-carbon dioxide relationships in the soil of an irrigated, California date orchard in 1943. Under the customary irrigation practice, they observed that the CO_2 content of one to six percent was high enough to affect appreciably the reaction of a calcareous soil. It was stressed that without adequate control of the partial pressure of CO_2 , pH values obtained on samples of that soil in the laboratory would be of questionable meaning in relation to plant responses. Even determinations made "in situ" might not represent true equilibrium conditions".

The most significant study of CO_2 effects on soil reaction was presented by Whitney and Gardner (63) in 1943. pH determinations by use of the Beckman pH meter and glass electrode were performed on suspensions of soil samples and samples of calcium and magnesium carbonates at equilibrium with varying partial pressures of CO_2 . The effects of dilution, aeration, and time of standing were studied. The following results were obtained:

1. Small changes in CO_2 pressure cause comparatively large changes in pH within the range of low CO_2 pressures comparable to those normally found in the soil.
2. The pH is approximately a straight-line function of the log of the CO_2 pressure in the pressure range from about 0.0003 to one atmosphere of CO_2 at constant moisture.
3. At constant CO_2 pressure the pH of soil suspensions tends to drop slightly with dilution.
4. The rise in pH of soils frequently observed with increasing water content probably is due primarily to dilution of the CO_2 absorbed in the soil sample.

5. The curves showing the effect of variations in CO_2 pressure on pH of the soils studied were similar in shape to curves for CaCO_3 but were affected more by dilution than were the curves for calcium or magnesium carbonate.
6. Curve positions are changed appreciably on the pH scale by the presence of calcium, magnesium, or sodium carbonates. The curves tend to group themselves into families depending upon the presence or the absence of one or more of these compounds.

(63:140)

Expressing the pH of soils as variable functions of the CO_2 pressure would better describe field conditions.

Determining two pH values for a soil, one at equilibrium with air and the other with pure CO_2 , would provide data to plot a curve characteristic of the soil.

Reed and Cummings (47) in 1945 discussed the concept mentioned above, and outlined a procedure for the determination of pH in soil suspensions to include CO_2 equilibration.

Gardner (22) in 1945 noted that pH varied directly with sodium percentages in soil, bentonite and calcite suspensions. The pH also increased with dilution. Comparatively low pH values for the Na-bentonite and high values for the calcareous soils indicated that the high pH of the latter may be more closely related to the hydrolysis of the carbonates than of the clay minerals. Carbon dioxide was not carefully controlled in the experiments, but all measurements were made under similar conditions.

Reuther and Crawford (49), in the course of soil

atmosphere studies in calcareous soils in 1947, confirmed the observations of Whitney and Gardner. By passing air-CO₂ mixtures containing one percent and ten percent CO₂ through soils adjusted to the moisture equivalent on Buchner funnels, they measured the effects of CO₂ pressure variations. At the low CO₂ concentrations, the pH values were 7.4 to 7.6. The pH changed to 6.8 to 7.0 when the same soils were brought to equilibrium with 10 percent CO₂.

Summary

The studies reviewed and many others relating to pH which cannot possibly be summarized in this paper provide only an introduction to CO₂ equilibria relations occurring in soils. The work of Whitney and Gardner set the stage for effective evaluation of a soil system, not at one equilibrium, but in the range of equilibria likely to occur under field conditions. Much of the data gathered in efforts to determine the effects and interactions of type of clay mineral, calcium carbonate, sodium, gypsum and soluble salts on pH are subject to question. Control of the important carbon dioxide variable was seldom attempted. The effects of the factors mentioned above on soil pH at CO₂ equilibrium have not been adequately studied. The marked effects of CO₂-pressure variations on pH have been observed and warrant full consideration

and control of CO_2 pressure in pH studies of soils.

Interpretation of the results of such studies in terms of CO_2 equilibria is particularly desirable when calcareous soils are involved.

Chapter III

METHODS AND MATERIALS

To determine the relationship of soil pH at CO₂ equilibrium to important variables in the soil system, the problem was studied in three phases:

1. A series of preliminary studies with six soils to develop a suitable apparatus and procedure, and to determine rates of equilibration at low and high CO₂ pressures.
2. Carbon dioxide equilibria studies of clay systems and chemical compounds to evaluate the influences of: type of clay mineral, sodium, calcium carbonate, sodium chloride and gypsum on pH.
3. Carbon dioxide equilibria studies of twelve Grand Junction Area soils, including determination of some physical and chemical characteristics of the soils, and the diagnosis and evaluation of the soils on the basis of equilibrium-pH data.

Preliminary studies

The primary objective of the initial study was the development of an apparatus and procedure for conducting CO₂ equilibria studies. The essential requirements for the technique were:

1. A constant supply of CO₂-air mixtures.
2. A convenient and rapid method of analysis of the gas supply for CO₂ pressure.
3. Constant temperature.
4. Containers for the suspensions which could be adapted to equilibration as well as pH determination.

Carbon dioxide was obtained from a tank of compressed CO_2 equipped with pressure reducing valves. The air- CO_2 mixtures were made in an air compressor of the type used in gasoline service stations and previously used in the CO_2 studies of Whitney and Gardner (64). The tank was filled with air from outside of the laboratory to a pressure of nearly 120 pounds per square inch. In the early stages of the study, the tank supply was used until exhausted (about three days). It was eventually found more desirable to fill the tank occasionally to maintain a good pressure in the line. This was necessary for more uniform equilibration of the samples. During the final twelve hours of equilibration the supply was not replenished and remained sufficiently constant in pressure. In the later studies, gas mixtures of CO_2 and air were prepared merely by passing CO_2 into the compressor tank until the desired mixture was obtained. It was found that approximately one percent CO_2 was made by passing the pure gas into the air tank at 10 pounds pressure for about 40 seconds. Ten percent CO_2 was obtained by the same procedure except the time was extended to two and one-half minutes. In both cases, the tank was allowed to complete filling automatically with air to 120 pounds pressure.

The CO_2 pressure of the gas mixtures was determined by the method of Wilson, Orcutt and Peterson (65).

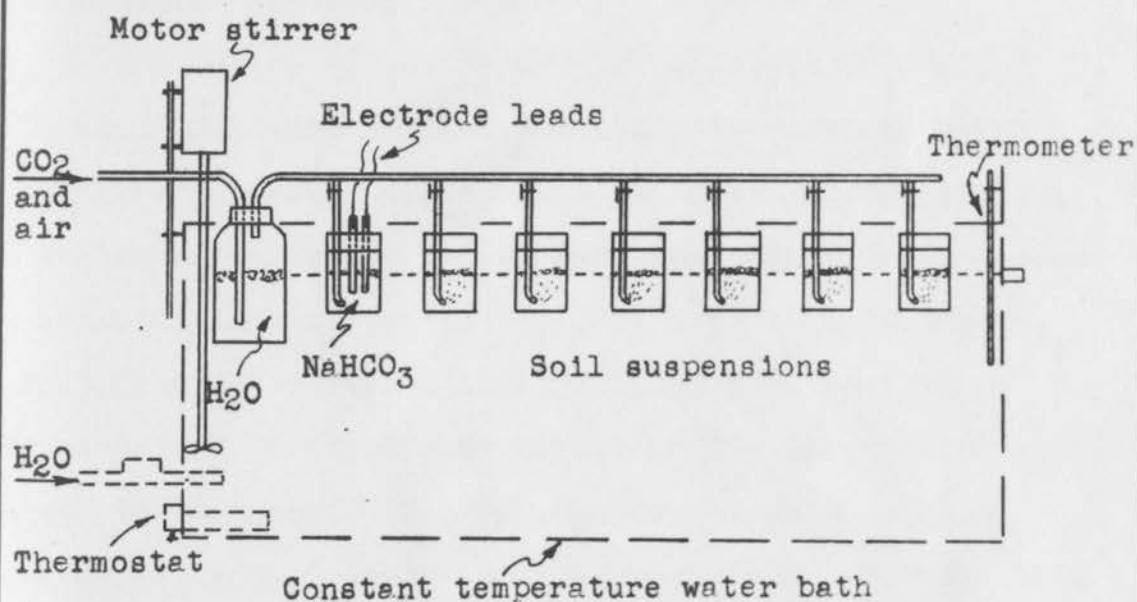
This method was very well adapted to use during the studies owing to its simplicity, rapidity and constant-reading attributes.

A constant temperature of 20°C , plus or minus 0.1° was maintained in the soil and clay systems during the equilibrations by use of a large rectangular, automatically controlled water bath.

Ordinary half-pint, wide-mouth glass jars were chosen as suspension containers. They were fitted with large rubber stoppers in which three holes had been cut. One hole was large enough to allow tight fitting of a specially prepared, sintered-filter, glass bubbler. The other two holes held snugly the large glass and calomel electrodes of a Beckman pH meter (Model G, glass electrode). One of the undesirable features of the bubblers was the clogging which occurred when bubbling ceased. Another was the difficulty in constructing the filters to operate uniformly. In the later stages of the clay system studies, the glass bubblers were replaced with stainless steel, gas dispersion bubblers (Micro Metallic Corp., Brooklyn, New York). However, these disc-type bubblers also presented clogging and cleaning difficulties. In some cases, disturbance of the soil particles in the jars was insufficient by bubbling to maintain dispersion; equilibration was not entirely satisfactory without frequent agitation by hand. A battery of six to eight of the

glass jars containing soil or clay suspensions were fitted with the stoppers and bubblers and clamped into place in the water bath at one time. One jar contained the sodium bicarbonate test solution. The gas from the supply tank was first passed through a reducing valve (Hoke-Phoenix regulator, 615V) to a bottle containing distilled water. The saturated gas continued through a compound outlet equipped with stopcock leads into the bubblers. All connections were completed with rubber and glass tubing. The apparatus is illustrated in Figure 1.

The technique of equilibration and pH determination adopted for all studies was as follows. A gas mixture of predetermined CO_2 pressure was introduced into the systems and allowed to bubble continuously through the suspensions. At periodic intervals, generally four to six hours during the day when the CO_2 pressure was low and every hour or two when the pressure was high, bubblers were stopped individually. The electrodes of the pH meter were immediately inserted and the pH of the suspension observed and recorded within 30 seconds. Barometric pressure and temperature in the laboratory were recorded whenever a set of pH readings were taken. When successive pH readings checked within 0.05 unit, equilibrium was considered attained. A new gas mixture was then prepared and the procedure repeated with a different, known partial pressure of CO_2 . The volume of the suspensions in the



Sintered-filter
glass bubbler

Disc-type
bubbler

Soil suspension container
with bubbler and electrodes

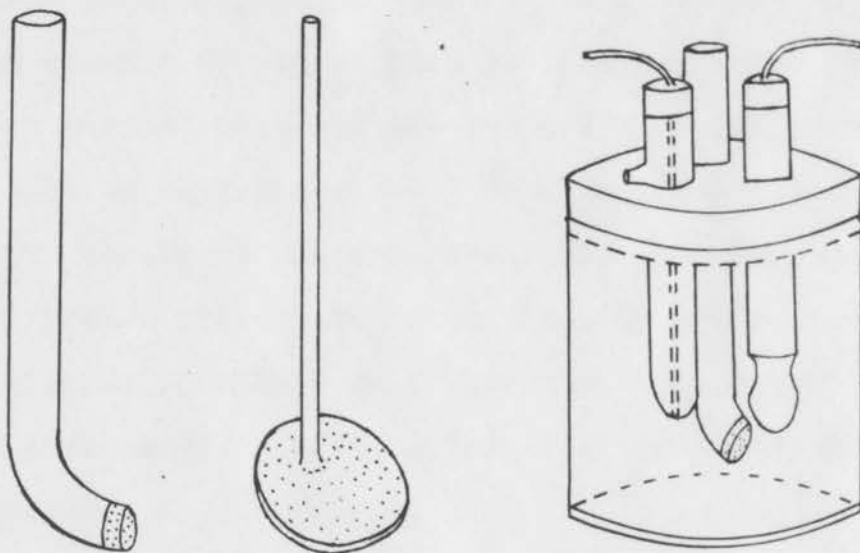


Fig. 1.--Carbon dioxide equilibration apparatus used in the studies of soils and clays.

jars was marked and maintained by addition of distilled water whenever necessary.

A series of simple studies with six Colorado soils were initiated to determine the time necessary for equilibrium pH values to be attained in soil suspensions and the characteristics of CO₂ equilibration. Twenty grams of each soil were placed in the jars and 100 milliliters of distilled water were added. Following initial pH determinations, a continuous stream of CO₂ was bubbled through the suspensions. The pH of each system was observed frequently to follow the progress of equilibration. When equilibrium pH values were attained in the suspensions, the CO₂ supply was cut off and air containing about 0.03 percent CO₂ was bubbled through the systems. Again the progress of equilibration was followed, this time for a much greater period of time until equilibrium was evident. A second series of the six soils in suspensions having a soil to water ratio of 1 to 5 were prepared. The previous treatment was reversed. The suspensions were equilibrated first with air of low CO₂ concentration. When equilibrium pH values were observed, CO₂ was bubbled through the suspensions and the "rate" of equilibration again studied.

Equilibria studies of clay systems

Samples of bentonite, kaolin, the Fort Collins

loam soil (upper six inches) from the Colorado Agricultural and Mechanical College experiment station farm, and another soil, sample number 57A, from an area near Grand Junction, Colorado were chosen for the clay system studies. A detailed description of the methods followed in preparing and handling one micron (upper size limit) clays for each material are given in Appendix A, titled Outline of Methods.

In summary, fractionation of all but the bentonite materials was accomplished by dispersion in tap water, sedimentation in 18-liter carboys, siphon removal of the clay fraction remaining in suspension at predetermined dates, flocculation of the clay by adjusting the pH of the suspensions to 5.0, and removal of excess solution by siphoning and finally filtration on Buchner funnels. The bentonite clays were obtained by centrifugation of one-percent suspensions in a Sharples supercentrifuge. The volume of the suspensions was reduced by slow evaporation in large dishes on a hot plate. The samples were not allowed to become completely dry.

Approximately 60 grams of each of the moist clays were dispersed by prolonged stirring in 500 milliliters of normal solutions of sodium and calcium chlorides. The solutions were mixed in various ratios, e.g. 5 parts of 1 N. NaCl to none of CaCl_2 , or 4 parts of 1 N. NaCl to 1 of 1 N. CaCl_2 . The clays were allowed to stand over-

night in the solutions, filtered on Buchner funnels and rewashed again with the chloride solutions until a total of 1500 milliliters were used for each 60 grams of clay. The treated clays were then dispersed and washed by stirring in 500-milliliter portions of 95 percent ethanol, and leached on Buchner funnels until the specific resistance of the leachates passed above 200,000 ohms. The washed samples were stored in glass-stoppered bottles, from which sufficient material was withdrawn as needed to make up exactly two-percent suspensions of the clays in distilled water. This percentage was chosen due to the limiting thixotropic properties of the bentonite.

Total exchange capacity and exchangeable bases were determined using aliquots of the clay suspensions. Exchange capacity was determined by a semi-micro adaptation of the ammonium acetate method developed by Shollenberger and Simon (53). Exchangeable sodium was determined by a modification of the method of Dobbins and Byrd (15). Calcium was determined by a macro-method outlined by the Regional Salinity Laboratory (62:114).

Equilibration studies of the clays were initiated by placing 30 milliliters of each of the six suspensions of the bentonite group in 100-milliliter, wide-mouthed glass jars fitted with stoppers and bubblers and mounted in the constant temperature water bath (Figure 1). Initial pH readings were taken, and a gas

mixture containing approximately 0.06 percent CO_2 was bubbled continuously through the suspensions. The pH readings were taken frequently during a 48-hour period, or for such additional or less time as proved necessary to attain equilibrium. The CO_2 content of the air in the pressure tank was then increased by passing pure CO_2 into the tank, and equilibration of the samples repeated at the new partial pressure of CO_2 in the gas mixture. The procedure was repeated at a third partial pressure of CO_2 , and finally with CO_2 gas alone. Thus a total of four equilibrium pH values for each suspension was obtained.

Fifty milligrams of Baker's chemically pure calcium carbonate were then added to each suspension to provide clay- CaCO_3 - CO_2 - H_2O systems, and equilibration at four levels of CO_2 partial pressure repeated. The amount of calcium carbonate added was determined on the basis of the data of Frear and Johnston (20) to provide a reasonable excess of solid-phase CaCO_3 in the systems at all CO_2 pressure levels.

One milliequivalent of sodium chloride was next added to each suspension to obtain the system clay- CaCO_3 - NaCl - CO_2 - H_2O . Equilibration at four levels of CO_2 partial pressure was repeated.

Lastly, 300 milligrams of Baker's C. P. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were added to the suspensions to obtain the

system clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O . Equilibration at four levels of CO_2 partial pressure was repeated. The amount of gypsum added was predetermined by best approximation based on the data of Frear and Johnston (20), to provide an excess of solid-phase gypsum in the systems at all times.

The barometric pressure and temperature in the laboratory were continuously observed with the pH determinations. The CO_2 pressure of the gas mixtures was checked before and after each set of pH readings, and the average value used. The volume of the suspensions was maintained at 30 milliliters by the addition of distilled water whenever necessary.

Equilibria studies of soils

Twelve soils, collected by field technicians of the Soil Conservation Service (see Acknowledgment) in a Western Slope Area of Colorado near Grand Junction were chosen for the studies. The location and description of sampling areas, and some physical and chemical characteristics of the soils were summarized in a report of an earlier study of the soils in 1946 at the Colorado Agricultural Experiment Station (19).

The soil samples were air-dried and passed through a two-millimeter sieve. Some rapid, approximate methods of analysis were performed on the samples to

obtain supplementary information of the physical and chemical characteristics of the soils. Soil texture was determined by the hydrometer procedure. The following analyses were performed in accordance with Regional Salinity Laboratory recommendations (62:86-99):

1. Saturated soil pastes were prepared. Determinations of pH, percent total soluble salts and moisture were completed on the pastes.
2. Saturation extracts were taken from the pastes on Buchner funnels. Determinations of pH, total soluble salts by conductivity, and soluble and exchangeable sodium were completed on the extracts.

An estimation of the amounts of gypsum present in the samples was gained by following the rapid procedure of Bower and Huss (7). An estimation of lime was obtained by acid neutralization (62:93).

Five grams of each soil were placed in the equilibration jar and brought into suspension with 25 milliliters of distilled water. Initial pH values were taken, and equilibration with four different air-CO₂ mixtures performed. Thus an equilibrium pH value for each of four different partial pressures of CO₂ was obtained for each soil.

The effect of dilution was investigated on six samples by preparing 0.6 grams of soil in 30 milliliters of water for a 1 to 50 soil to water ratio. The suspensions were equilibrated at four levels of CO₂ partial pressure.

Samples of the twelve Grand Junction Area soils were subjected to a period of leaching by following somewhat closely a method of permeability determination outlined by the Regional Salinity Laboratory (62:123-24). To follow the progress of removal of soluble salts, the conductivities of the initial and succeeding leachates were measured by use of a two-milliliter, pipette type conductivity cell and Model RC-1 International Instrument Company conductivity bridge. An arbitrary end-point of approximately 6500 ohms specific resistance (about 100 parts per million soluble salts in solution) was chosen. Leaching was prolonged sufficiently to attain this value. The experiment was conducted in a constant temperature room at 22°C. It was necessary to transfer samples 13A, 16A and 45C to Buchner funnels for leaching to reduce the salt concentration in line with the other samples. The leached samples were air dried, ground to pass the two-millimeter sieve, and equilibrated at four levels of pCO_2 in suspensions having a soil to water ratio of 1 to 5 to obtain data for pH curves.

An approximation of the amounts of soluble salts removed from the soils by leaching was obtained by conductivity determinations of composite samples of the accumulated leachates of each soil, brought to convenient volume and expressed on a milligram per hundred grams of soil basis(19, 62).

Chapter IV

ANALYSIS OF DATA

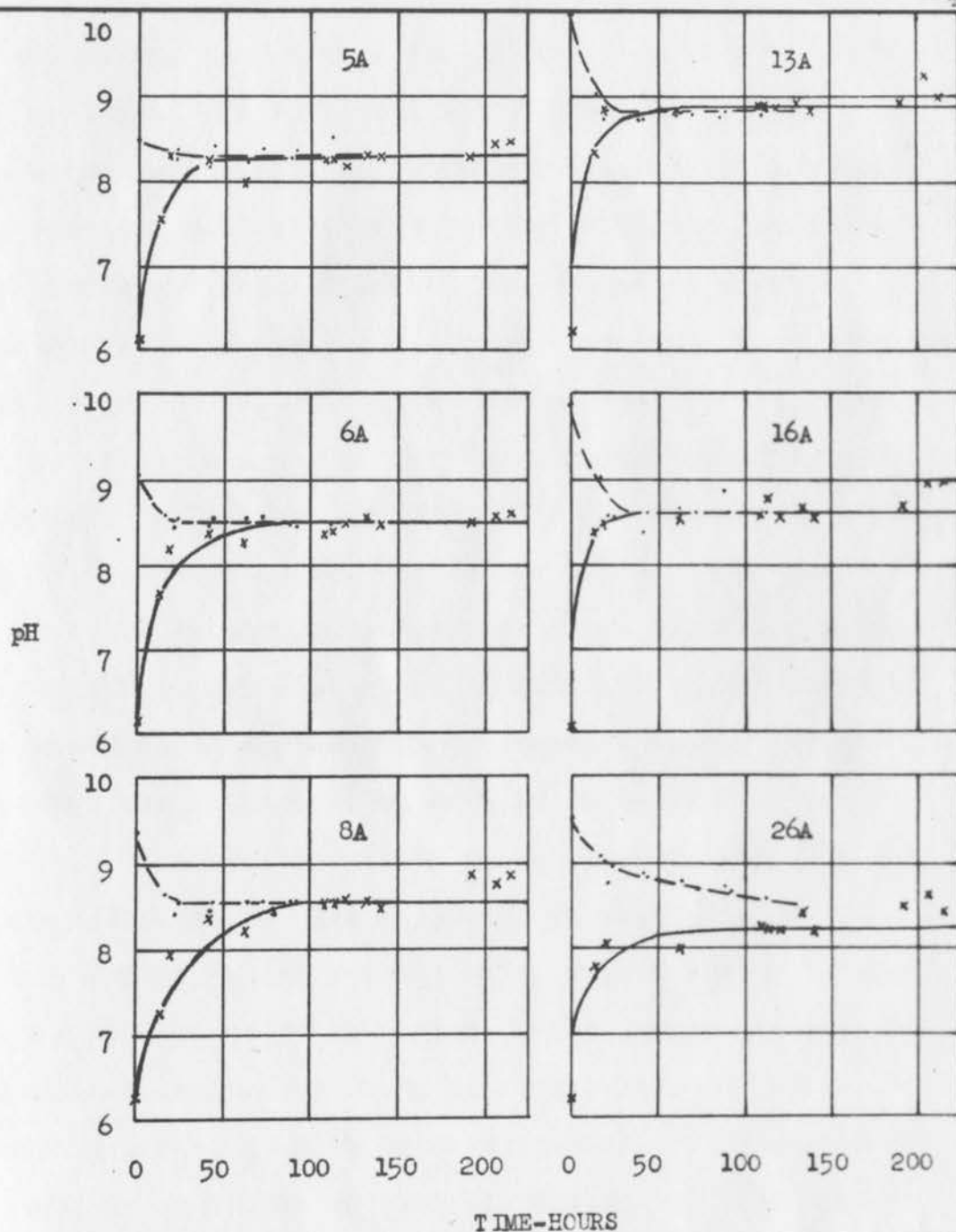
The collection of data to determine the relation of the pH of soils in equilibrium with carbon dioxide to several variables in the soil system extended over the sixteen-month period, March 1948 to June 1949. Inasmuch as the study was performed in three separate phases, the data will be presented in this chapter under three headings:

1. Preliminary studies.
2. Clay system studies.
3. Soil system studies.

Preliminary studies

The time necessary to attain an equilibrium pH value in a soil suspension when a gas mixture of known, constant CO₂ partial pressure is bubbled through the system varies with the CO₂ pressure. In Figures 2 and 3, the observed pH values in soil suspensions having a soil to water ratio of 1 to 5 were plotted against the time in hours during the equilibration period for each soil.

Equilibrium pH values with air containing less than 0.05% CO₂ was attained within a 48-hour period in all but two cases, as indicated in Figure 2. In the cases



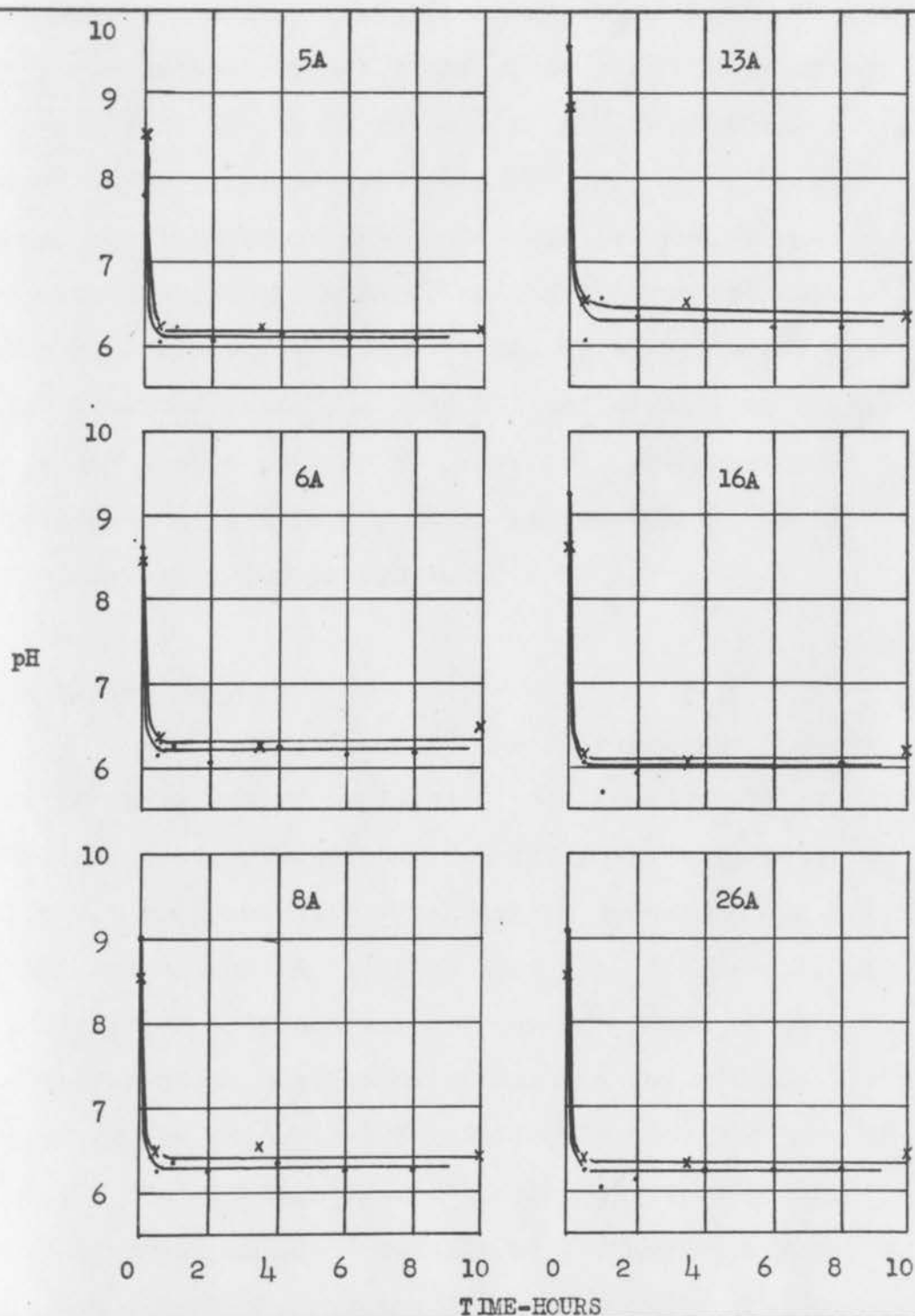
--- SYSTEM NOT PREVIOUSLY EQUILIBRATED
 —x— SYSTEM PREVIOUSLY EQUILIBRATED WITH PURE CO₂

Fig. 2.--Time required for equilibrium between soil systems and air at 20°C.

[The soil to water ratio was 1 to 5. The soil sample number is indicated, e.g. 5A]

of samples 8A and 26A the time necessary for equilibrium was prolonged due to defective bubbling and clogging of the bubblers. Little difference in time existed between the samples previously equilibrated with CO_2 and those not previously equilibrated. Regardless of previous treatment, the suspensions showed leveling off at constant equilibrium pH values. After the 48-hour period, variations of as much as 0.2 to 0.3 pH units occurred, due largely to slight variations in the partial pressure of CO_2 in the gas supply. Variations of this type were found to be rather common at such a low partial pressure of CO_2 . The advisability of equilibrating samples with gas mixtures of air and CO_2 of somewhat higher CO_2 partial pressure was indicated, especially in later studies.

The time necessary for equilibrium between the suspensions and CO_2 was rapid and apparently complete within several hours, as indicated by the curves of the graphs in Figure 3. An initial rapid drop below equilibrium level seemed to occur at first, followed by a leveling off as equilibrium was reached. The samples previously equilibrated with air seemed to level off at an equilibrium pH value about 0.1 pH unit higher than those which had not been equilibrated with air. The significance of this event was questioned, considering the limited data and variability in technique in this early study. It was not justified in later studies.



--- SYSTEM NOT PREVIOUSLY EQUILIBRATED

—x— SYSTEM PREVIOUSLY EQUILIBRATED WITH AIR

Fig. 3.--Time required for equilibrium between soil systems and pure CO_2 at 20°C .

[The soil to water ratio was 1 to 5. The soil sample number is indicated, e.g. 5A]

In summary, it seemed that the time necessary to reach equilibrium pH values in soil suspensions with air of low CO₂ content was within 48 hours. With CO₂ alone, equilibrium is attained within several hours. No permanent change in pH is caused by such treatment. Later experience with the more dilute clay suspensions (clay to water ratio was 1 to 50) indicated that equilibrium pH values even at the lower CO₂ pressures were attained in 4 to 6 hours, and less time was required with increasing CO₂ pressure.

Clay system studies

Analyses of each of the clay suspensions were made for base exchange capacity, sodium and calcium. The average results of duplicate analyses are summarized in Table 5. The bentonite clay systems contained the greatest amounts of sodium and calcium, the sum of these cations averaging 102 milliequivalents per 100 grams of clay. The preferential adsorption of calcium was evident by comparing the original treatment ratio with the percent sodium. The exchange capacity determinations by the neutral normal ammonium acetate method gave lower values than the sum of the cations indicated. This also occurred in the case of the Fort Collins clay and the 57A clay, but the reverse was true in the case of the kaolin clays. It must be borne in mind that the "clays" referred to

Table 5.--SUMMARY OF ANALYSES OF CLAY SUSPENSIONS

¹ Treat- ment ratio	² Sus- pension percent	m.e.Na per 100 g. clay	m.e.Ca per 100 g. clay	Sum Na + Ca	Percent Na	³ Exchange capacity m.e./100g.
<u>Bentonite clay suspensions</u>						
5Na:0Ca	2.085	94.3	4.3	98.6	96	⁴ 92.3
4Na:1Ca	1.993	62.6	43.9	106.5	59	98.0
3Na:2Ca	2.044	17.0	74.6	91.6	19	96.2
2Na:3Ca	2.000	9.6	91.8	101.4	9	96.0
1Na:4Ca	2.043	7.9	96.4	104.3	8	96.5
0Na:5Ca	2.008	6.0	104.1	110.1	5	96.4
Average				102.1	..	96.6
<u>Fort Collins clay suspensions</u>						
5Na:0Ca	2.016	66.7	7.4	74.1	90	59.9
4Na:1Ca	2.001	25.7	40.0	65.7	39	59.5
3Na:2Ca	2.002	7.9	51.7	59.6	13	59.6
2Na:3Ca	1.994	6.2	55.7	61.9	10	59.7
1Na:4Ca	2.001	5.0	59.0	64.0	8	59.5
0Na:5Ca	2.000	0.2	61.0	61.2	<1	59.9
Average				64.4	..	59.7
<u>Soil 57A clay suspensions</u>						
5Na:0Ca	2.000	33.8	3.8	37.6	90	41.4
6Na:1Ca	2.017	19.9	19.8	39.7	50	41.4
4Na:1Ca	2.000	17.1	26.3	43.4	39	39.4
3Na:2Ca	2.013	9.6	34.0	43.6	22	39.6
1Na:4Ca	2.021	2.4	35.1	37.5	6	37.4
0Na:5Ca	2.000	1.2	38.8	40.0	3	36.6
Average				40.3	..	39.3
<u>Kaolin clay suspensions</u>						
5Na:0Ca	2.006	4.1	0.0	4.1	100	5.4
6Na:1Ca	2.009	1.5	2.5	4.0	37	5.0
4Na:1Ca	1.997	0.4	3.1	3.5	12	5.3
3Na:2Ca	2.002	0.4	3.8	4.2	9	5.2
1Na:4Ca	2.001	0.13	4.3	4.4	3	5.5
0Na:5Ca	2.001	0.08	3.8	3.9	2	5.3
Average			...	4.0	..	5.3

¹Parts 1 N. NaCl to 1 N. CaCl₂ used to wash clays.

²A 2% suspension represents 2 grams of clay per 100ml.

³Determined by ammonium acetate procedure (53).

⁴Omitted from average due to loss of clay in method.

represent the separates having particle sizes less than one micron in diameter. The average sum of cations in the Fort Collins clay suspensions was 64 milliequivalents per 100 grams of clay, whereas the exchange capacity averaged about 60. In the 57A clay suspensions, the average sum of the cations sodium and calcium averaged about 40 milliequivalents per 100 grams of clay, and the exchange capacity was about 39 milliequivalents. The kaolin clay suspensions contained the least amounts of sodium and calcium, the sum of the cations averaging 4 milliequivalents per 100 grams of clay, and the exchange capacity was about 5 milliequivalents.

It was difficult to obtain a good variation of sodium percentages among the clays. The treatment ratios were changed after the experience of the first two groups of clays to provide a better variation, but results were not as satisfactory as desired. Lack of time and materials precluded preparation of additional samples. Nevertheless, a range of sodium percentages from 100 to less than one was obtained.

Equilibria pH and pH curves.--A summary of the detailed data collected in determining the effects of type of clay, sodium, calcium carbonate, sodium chloride and gypsum on pH at equilibrium in the clay suspensions with known, constant partial pressures of CO₂ has been included in the Appendix B, Tables A to E inclusive.

Table A is a sample data sheet, showing how the individual pH readings were recorded during CO₂ equilibration at the four different levels of CO₂ partial pressure. Tables B, C, D, and E summarize the data sheets of systems of the same type of clay. These equilibrium pH values were plotted against the logarithm of the corresponding partial pressure of carbon dioxide used. Graphs of the type illustrated in Figure A of Appendix B were constructed for each system, to obtain characteristic pH curves. A summary of the curves is presented in Figures 4, 5 and 6. The pH curves of twelve Grand Junction Area soils, plotted from detailed data obtained in a later study, are included at this point for convenience in comparisons. In addition the pH curves of the "check" systems of Baker's C.P. calcium carbonate have been plotted with the clay systems. A few general remarks from observation of the curves are noted at this time:

1. The pH values for corresponding log values of the partial pressure of CO₂ at equilibrium fit an average straight-line curve in all systems. Largest variations of observed pH values from the average curves occurred at the lowest CO₂ pressures. In many cases, variation from the curves did not exceed 0.05 pH unit.
2. Pronounced differences between the clays are not apparent from observation. However, there seems to be a tendency for the bentonite and Fort Collins clays to occupy a somewhat higher position on the pH scale than the 57A and kaolin clays.
3. The pH curves of the clay systems containing the greater amounts of sodium occupy generally higher positions on the pH scale than those predominating in calcium.

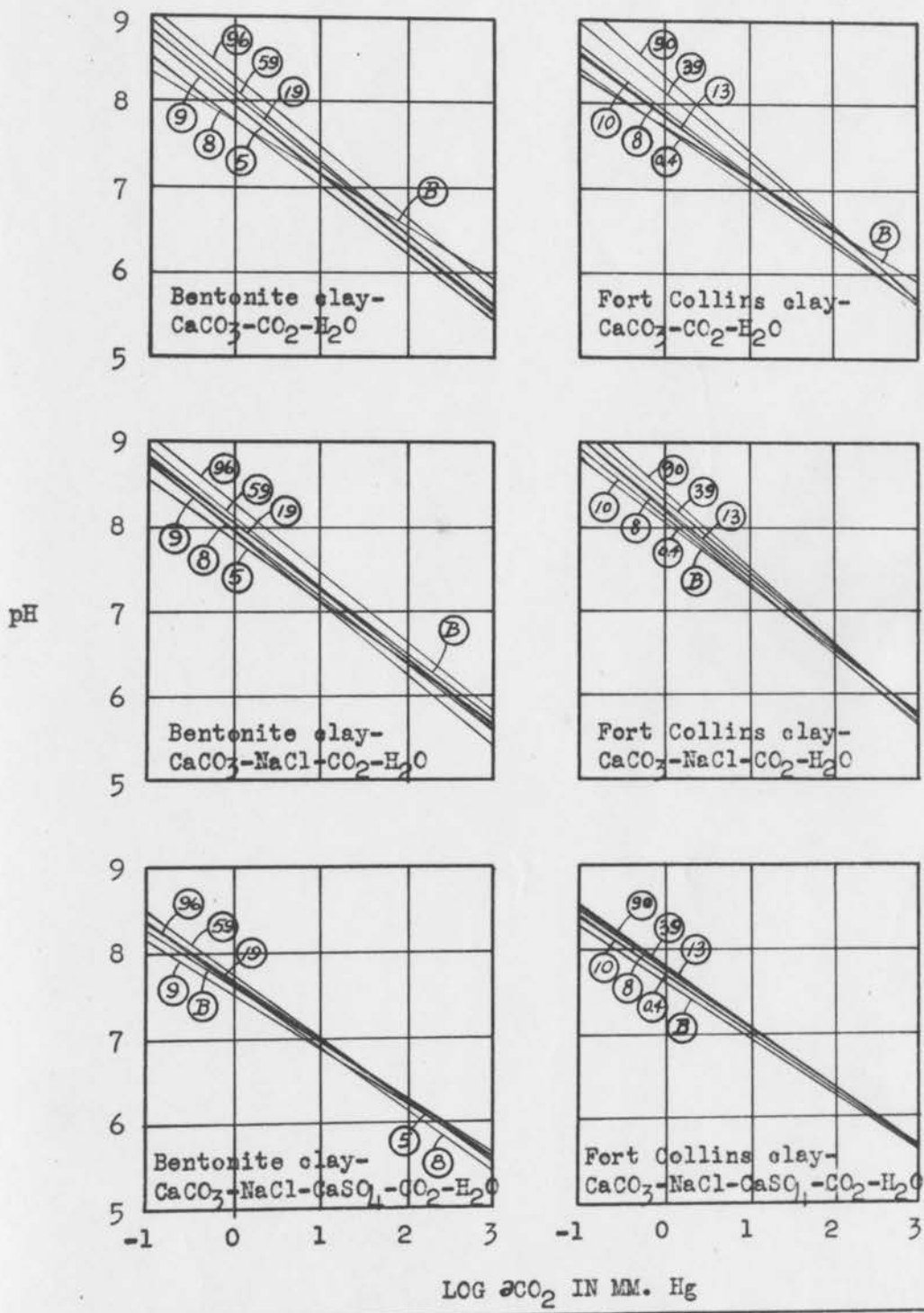


Fig. 4.--The pH curves of bentonite and Fort Collins clay systems at 20°C.

[Percent sodium of sum of cations indicated.
Baker's C.P. CaCO₃ systems labeled B]

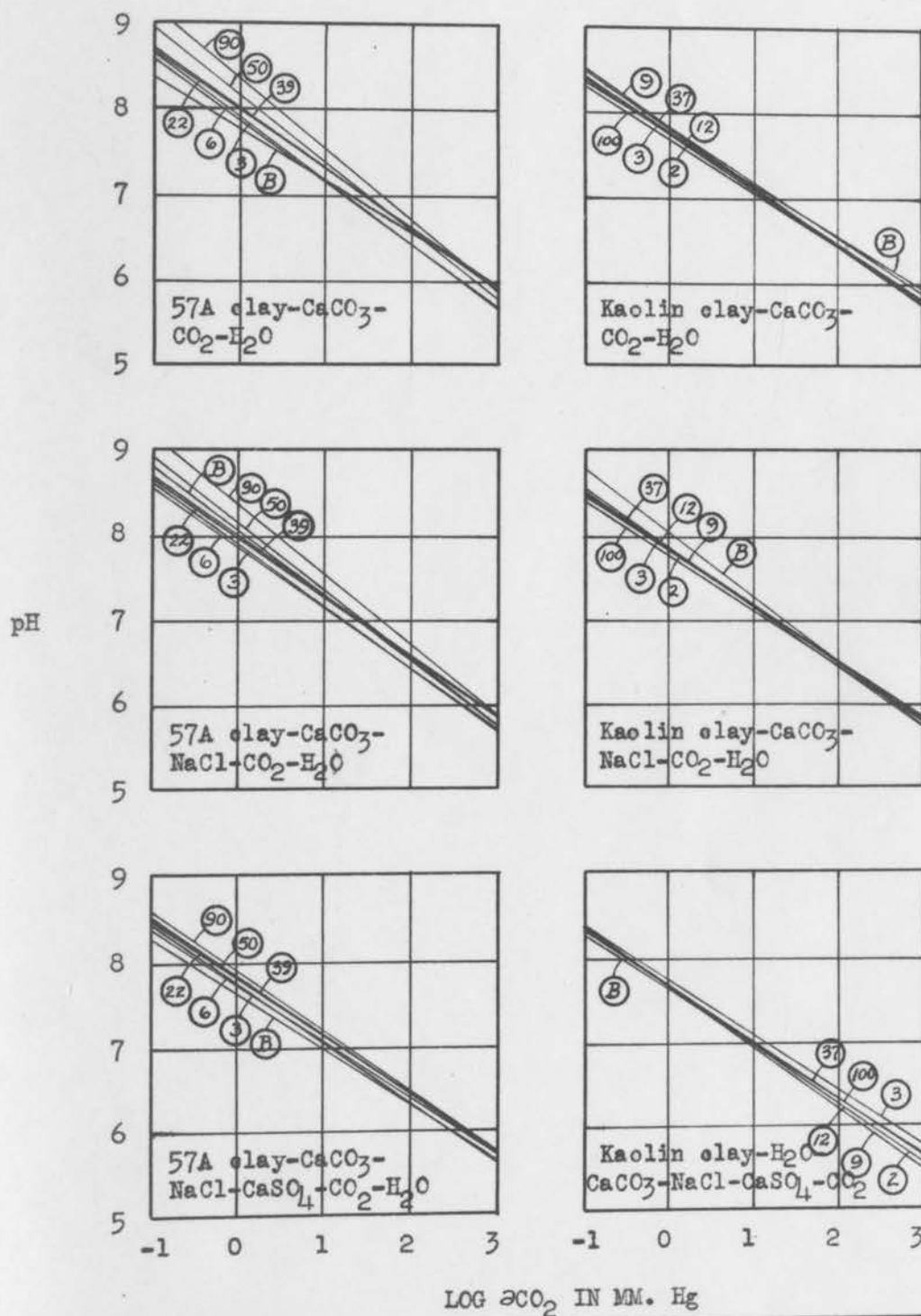


Fig. 5.--The pH curves of 57A and kaolin clay systems at 20°C.

[Percent sodium of sum of cations indicated.
Baker's C.P. CaCO_3 systems labeled B]

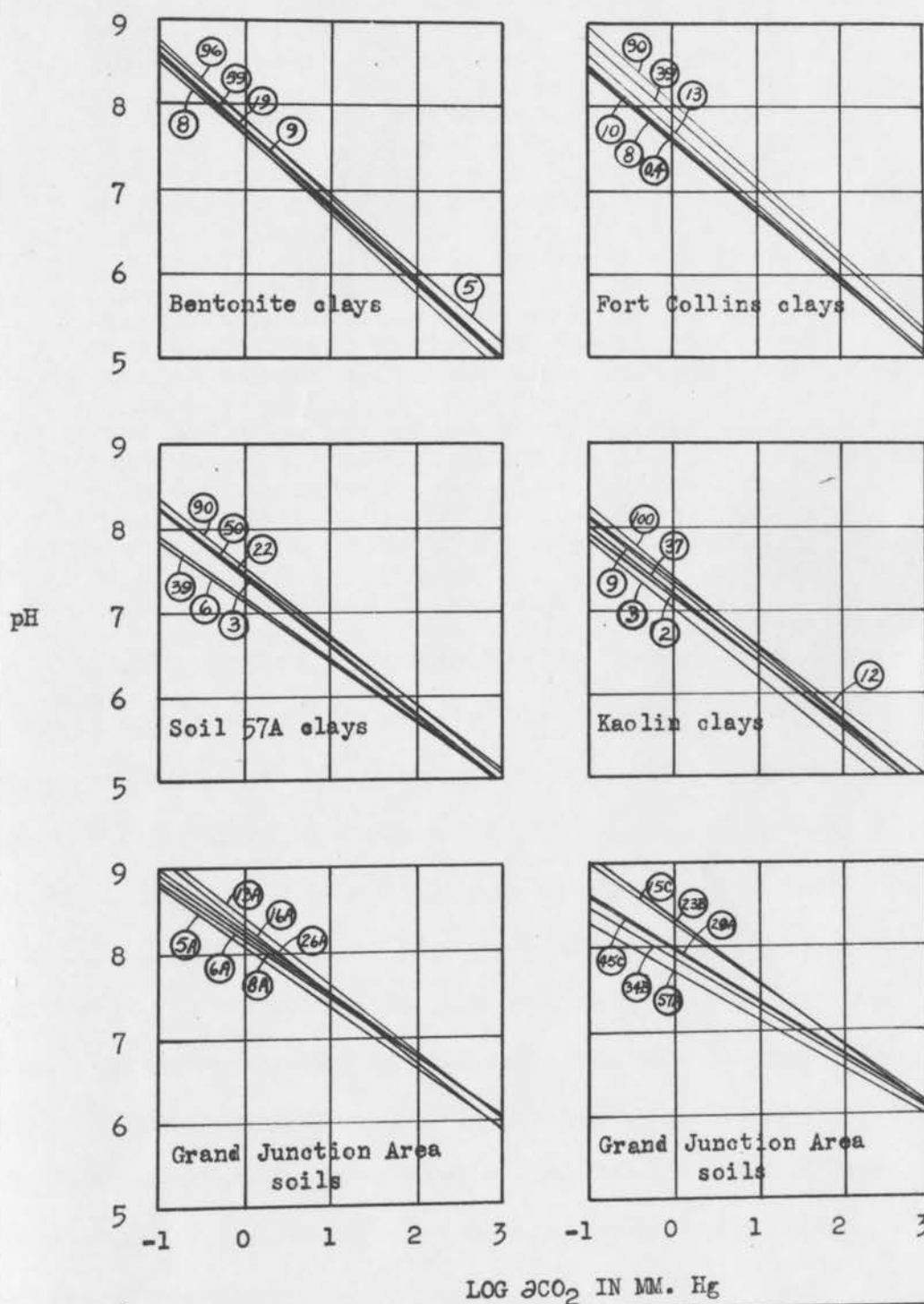


Fig. 6.--The pH curves of clays and soils at 20°C.

[Percent sodium of sum of cations indicated for the clay systems. Soil sample numbers indicated]

4. The addition of calcium carbonate to the clay systems resulted in a displacement of the pH curves in most instances to higher positions, as well as a noticeable though slight lessening of the slopes of the curves.
5. The addition of sodium chloride to the systems did not seem to produce any pronounced effect, except for a somewhat closer grouping of the pH curves within the same type of clay.
6. The addition of gypsum produced a marked change in the grouping and positions of the curves, all dropping more or less sharply on the pH scale, but with little noticeable change in slope.
7. The pH curves of the Baker's CaCO_3 systems show greatest variation from the clay systems before the addition of sodium chloride and gypsum, occupying a lower position on the pH scale at the low CO_2 pressures, but with gentler slope and higher position in pH at high CO_2 pressures. In the CaCO_3 systems containing sodium chloride and gypsum, the curves all appear somewhat similar in position and slope.

The effect of changing CO_2 pressure on the pH of clays was better illustrated by plotting pH against the atmospheres of CO_2 pressure. This is presented in Figure 7, for clay systems of both high and low sodium content. The particularly rapid changes which occur in pH in the lower range of CO_2 pressures are evident. The Fort Collins and bentonite clays occupy the higher positions, considering the curves with respect to pH. The kaolin clays occupy the lowest positions. In addition, the clays containing the higher amounts of sodium have the higher pH values at constant, corresponding CO_2 partial pressures.

It was necessary to select pH values from each system at a partial pressure of CO_2 constant through

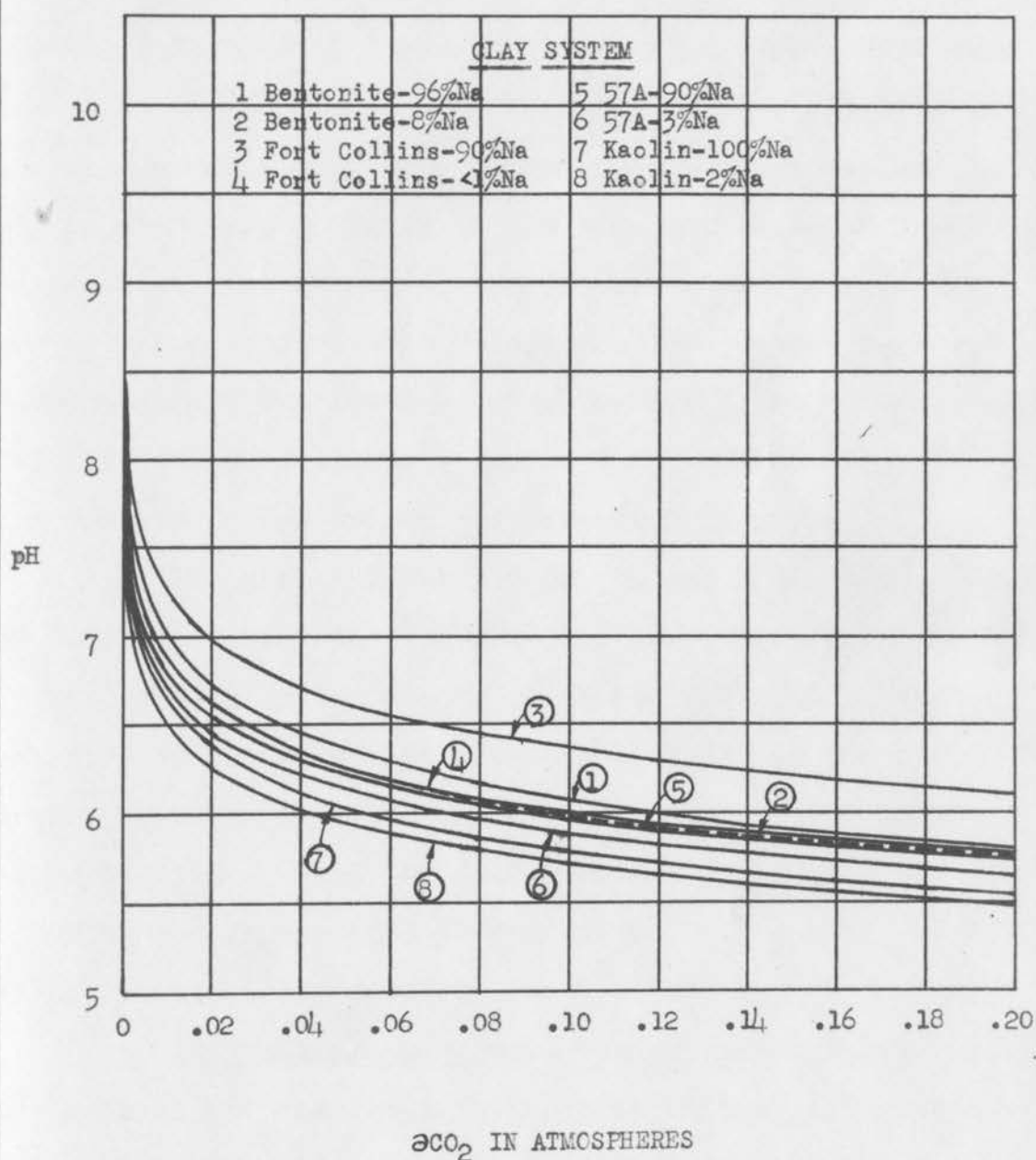


Fig. 7.--Effect of increasing CO_2 pressure on the pH of clay suspensions of high and low sodium content.

[The clay to water ratio was 1 to 50. The data were obtained from the pH curves of the clay systems. See Fig. 6]

all the systems for comparisons. From the straight-line curves in Figures 4, 5 and 6, the pH value for each system was taken at $-0.64 \log \partial \text{CO}_2$, representing the equilibrium pH value under a partial pressure of 0.0003 atmosphere of CO_2 in every case. These values are summarized in Table 6. In addition, the slopes of the pH curves were computed by use of the equilibrium pH values at 0.0003 atmosphere and one atmosphere CO_2 pressure, the corresponding values then being substituted in the formula: $b = \Delta \text{pH} / \Delta \log \partial \text{CO}_2$. The computed slope values are presented in Table 7.

The system Baker's CaCO_3 in water had a pH at 0.0003 atmospheres ∂CO_2 of 8.12; the pH curve of the system had a slope of 0.602. With the addition of sodium chloride in amount equivalent to that added to the clay systems, the pH changed to 8.51 and the slope of the pH curve to 0.761. When the system included both sodium chloride and gypsum, the pH changed to 8.06 and the slope of the curve became 0.659.

Statistical analyses.---Two of the more obvious criteria of differences existing between the clay systems appeared to be: (1) the pH at equilibrium with 0.0003 atmosphere partial pressure of CO_2 ; and, (2) the slope values of the pH curves. To derive the effect of differences in these criteria due to type of clay, sodium, calcium carbonate, sodium chloride and gypsum, it was necessary to subject the data to statistical methods.

Table 6.--THE pH OF CLAY SYSTEMS AT 20°C

ORIGINAL SODIUM PERCENT OF Na+Ca	SYSTEM			
	Clay-CO ₂ - H ₂ O	Clay-CaCO ₃ -CO ₂ -H ₂ O	Clay-CaCO ₃ -NaCl-CO ₂ -H ₂ O	Clay-CaCO ₃ - NaCl-CaSO ₄ - CO ₂ -H ₂ O
<u>pH of Bentonite clays</u>				
96	¹ 8.42	8.80	8.80	8.15
59	8.24	8.62	8.62	8.24
19	8.28	8.55	8.55	8.12
9	8.29	8.45	8.45	7.96
8	8.20	8.25	8.45	8.14
5	8.38	8.45	8.30	8.12
<u>pH of Fort Collins clays</u>				
90	8.61	8.90	9.03	8.29
39	8.47	8.67	8.88	8.27
13	8.28	8.35	8.79	8.30
10	8.18	8.42	8.65	8.17
8	8.15	8.34	8.76	8.25
1	8.12	8.19	8.66	8.19
<u>pH of Soil 57A clays</u>				
90	8.04	8.85	8.85	8.34
50	7.97	8.62	8.62	8.28
39	7.66	8.46	8.46	8.24
22	7.95	8.43	8.43	8.27
6	7.57	8.30	8.30	8.16
3	7.94	8.37	8.37	8.22
<u>pH of Kaolin clays</u>				
100	7.98	8.09	8.18	8.10
37	7.73	8.23	8.23	8.16
12	7.86	8.23	8.27	8.11
9	7.83	8.27	8.32	8.17
3	7.56	8.15	8.25	8.15
2	7.67	8.17	8.25	8.15

¹All pH values taken at equilibrium with 0.0003 atm. CO₂.

Table 7.--THE SLOPES OF THE pH CURVES OF CLAY SYSTEMS

ORIGINAL SODIUM PERCENT OF Na+Ca	SYSTEM			
	Clay-CO ₂ - H ₂ O	Clay-CaCO ₃ - CO ₂ -H ₂ O	Clay-CaCO ₃ - NaCl-CO ₂ - H ₂ O	Clay-CaCO ₃ - NaCl-CaSO ₄ - CO ₂ -H ₂ O
<u>Bentonite clays</u>				
96	¹ 0.929	0.818	0.818	0.696
59	0.929	0.824	0.824	0.724
19	0.909	0.804	0.804	0.693
9	0.906	0.787	0.787	0.639
8	0.875	0.776	0.830	0.736
5	0.872	0.795	0.727	0.699
<u>Fort Collins clays</u>				
90	0.892	0.872	0.909	0.719
39	0.886	0.810	0.870	0.707
13	0.875	0.744	0.844	0.722
10	0.844	0.759	0.815	0.688
8	0.858	0.733	0.849	0.707
<1	0.838	0.690	0.821	0.690
<u>Soil 57A clays</u>				
90	0.821	0.818	0.818	0.702
50	0.787	0.787	0.787	0.710
39	0.736	0.724	0.724	0.682
22	0.818	0.707	0.707	0.685
6	0.716	0.719	0.719	0.670
3	0.815	0.739	0.739	0.707
<u>Kaolin clays</u>				
100	0.866	0.628	0.670	0.673
37	0.810	0.679	0.679	0.693
12	0.787	0.682	0.685	0.696
9	0.821	0.688	0.716	0.730
3	0.835	0.645	0.662	0.645
2	0.778	0.673	0.685	0.707

¹the slope value "b" was calculated from $b = \Delta \text{pH} / \Delta \log \partial \text{CO}_2$, using data from Figures 4, 5 and 6.

The major questions which arose included determination of the probability that the systems might not be of equal character, and that the observed differences were not due to experimental error or chance fluctuations. The data as arranged in Tables 6 and 7 were suitable in many respects for an analysis of variance, but the factor of percent sodium was not uniform between the clay groups. Plotting the pH and slope data against sodium percent, then picking off new values for pH and slope at 100, 80, 60, 40, 20 and 0 percent sodium for each clay caused such leveling off of variations in the original data that the validity of the statistical analysis was modified. A trial analysis by this method was attempted, following closely an outline for analysis of variance given by Leonard and Clark (29:195-205), but when the homogeneity test was applied (29:206-207) the series proved too supernormal to admit that they resulted from a single population. In other words, the variability between clays was greater than that within clays.

Therefore, the data presented in Tables 6 and 7 were subjected to three types of statistical comparison methods for derivation of significant differences:

1. The effect of clay was studied by comparing clay groups according to an outline recommended by Leonard and Clark (29:62-64), and applying Fisher's "t" test.
2. The effect of sodium was investigated by measuring correlation between sodium content (milliequivalents per 100 grams clay) of the systems and the

pH and slope values. All the data was combined into one study. The particular limitation of this method was the extent of the data.

3. The effects of CaCO_3 , NaCl and gypsum were studied by applying some rapid approximate statistical procedures (rank methods) as outlined by Wilcoxon (63). First, the several treatments within each clay were compared for differences as a whole (63:6,7), and second, paired comparisons of the systems were made (63:5,6).

The results of the statistical analysis to determine significant differences between clay groups are summarized in Table 8. From observation of the t-values obtained, significant differences existed at either the 5% or 1% levels in many cases, with respect to both pH and slope of the pH curves. Significant differences could not be verified between bentonite and Fort Collins clays, or between bentonite and the 57A clays with respect to pH. Significant differences could not be established on the basis of the data between the 57A and kaolin clays with respect to slope of the pH curves.

The results of the correlation study to compare the sodium concentration of the original systems with pH and slope of the pH curves are given in Table 9. Highly significant correlations were obtained in all the systems but those which contained gypsum. To illustrate the correlations, the data were plotted in Figure 8. The pH values from Table 6 and the slope values from Table 7 were plotted against the milliequivalents per 100 grams of clay originally present in the systems (Table 5).

Table 8.--SUMMARY OF STATISTICS FOR COMPARISON OF CLAY SYSTEMS WITH RESPECT TO pH AND SLOPE OF pH CURVES

CLAY GROUP	FACTOR STUDIED					
	pH at 0.0003 atm. CO_2		Slope of pH curve			
	1_s	$2_{o\bar{x}}$	$3_{\bar{x}}$	s	$o\bar{x}$	$\bar{x}$
Bentonite----	.22	.04	8.37 $\pm$.04	.079	.016	-.800 $\pm$.016
Fort Collins--	.28	.06	8.46 $\pm$.06	.076	.015	-.798 $\pm$.015
57A-----	.32	.06	8.28 $\pm$.06	.050	.010	-.743 $\pm$.010
Kaolin-----	.21	.04	8.09 $\pm$.04	.066	.013	-.714 $\pm$.013

CLAY GROUPS	COMPARISONS OF STATISTICS	
	4t -value(pH)	t-value(slope)
Bentonite vs. Fort Collins--	1.257	0.089
Bentonite vs. 57A-----	1.242	2.992**
Bentonite vs. Kaolin-----	4.597**	4.081**
Fort Collins vs. 57A-----	2.099*	2.986**
Fort Collins vs. Kaolin----	5.253**	4.098**
57A vs. Kaolin-----	2.465*	1.729

$^1 s = \sqrt{\sum(x-\bar{x})^2/(N-1)}$ is the standard deviation, or standard error of a single observation.

$^2 o\bar{x} = s/\sqrt{N}$ is the standard error of the mean.

$^3 \bar{x} = \sum x/N$ is the mean.

$^4 t = [(\bar{x}_1 - \bar{x}_2)/s]\sqrt{N/2}$ is significant at 5% level if marked *, or at the 1% level if marked **.

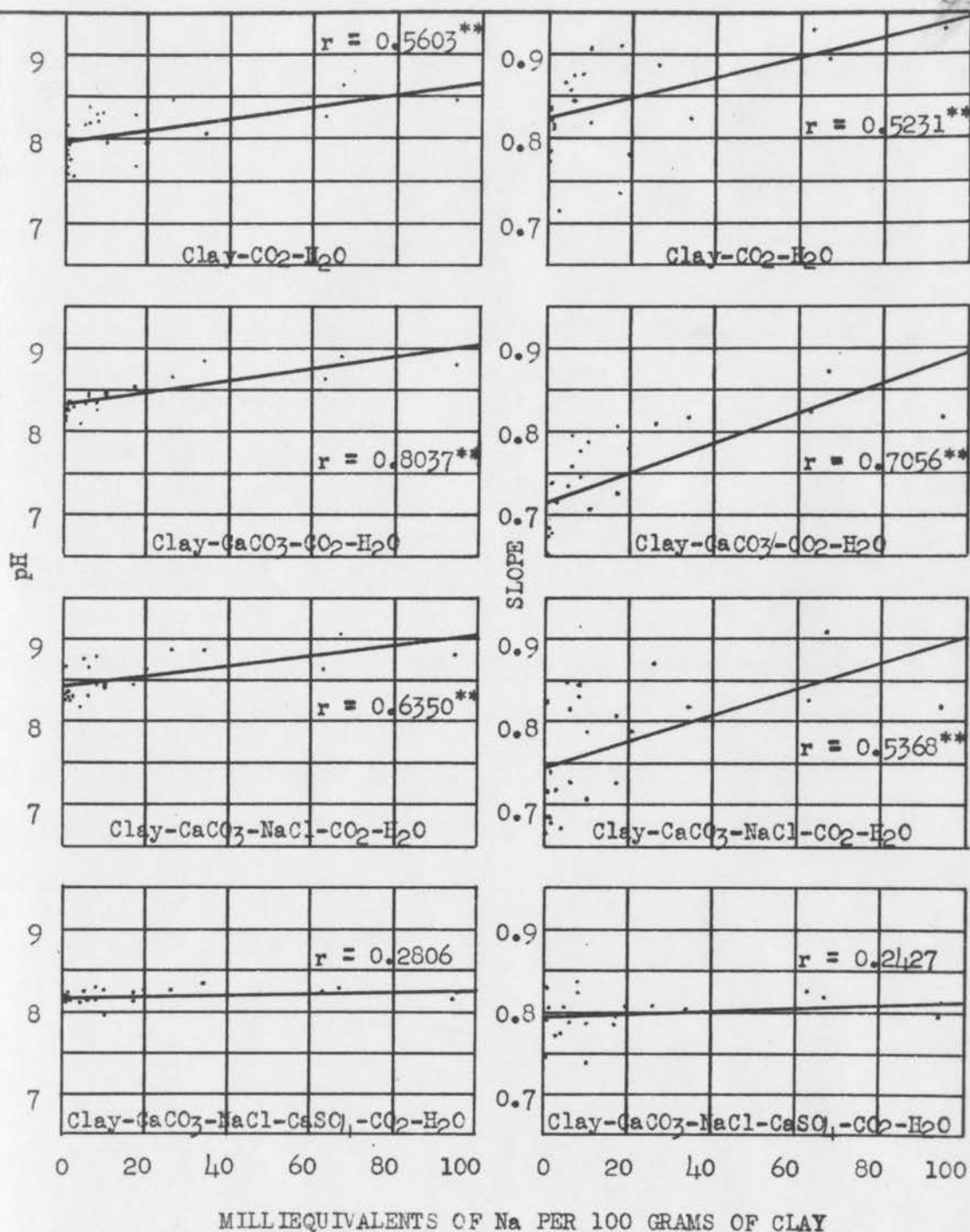


Fig. 8.--The pH and slope of the pH curve plotted against sodium content of clay systems.

[System and correlation coefficient indicated.
Data obtained from Tables 5, 6 and 7]

Table 9.--CORRELATION BETWEEN SODIUM IN CLAY SYSTEMS AND pH OR SLOPE OF pH CURVE

SYSTEM	COEFFICIENT OF CORRELATION BETWEEN	
	m.e.Na/100g.clay and pH at 0.0003 atmospheres ∂CO_2	m.e.Na/100g.clay and slope of pH curve
Clay-CO ₂ -H ₂ O -----	¹ 0.5603**	0.5231**
Clay-CaCO ₃ -CO ₂ -H ₂ O-----	0.8037**	0.7056**
Clay-CaCO ₃ -NaCl-CO ₂ -H ₂ O--	0.6350**	0.5368**
Clay-CaCO ₃ -NaCl-CaSO ₄ -CO ₂ -H ₂ O -----	0.2806	0.2427

The coefficient of correlation is significant at the 5% point if marked *, or at the 1% point if marked **.

Equations for the regression of pH and slope on milliequivalents of sodium per 100 grams of clay were calculated as outlined by Leonard and Clark (29:98). They were as follows, the symbol x indicating milliequivalents of sodium:

$$\text{System: clay-CO}_2\text{-H}_2\text{O: } \text{pH} = 7.95 + 0.0067x \\ \text{slope} = 0.822 + 0.0012x$$

$$\text{clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O:} \\ \text{pH} = 8.30 + 0.0074x \\ \text{slope} = 0.715 + 0.0018x$$

$$\text{clay-CaCO}_3\text{-NaCl-CO}_2\text{-H}_2\text{O:} \\ \text{pH} = 8.42 + 0.0063x \\ \text{slope} = 0.744 + 0.0016x$$

$$\text{clay-CaCO}_3\text{-NaCl-CaSO}_4\text{-CO}_2\text{-H}_2\text{O:} \\ \text{pH} = 8.17 + 0.0009x \\ \text{slope} = 0.693 + 0.0002x$$

These equations represent the best determination of values of pH or slope if the exchangeable sodium or sodium content

of the clay system is known. If, on the other hand, it is desirable to calculate the exchangeable sodium status of the clay (or sodium content of the system) when the equilibrium pH values or slope of the pH curve are known, then the data could be applied to regression equations of the form: milliequivalents of sodium on pH or slope.

Referring to the graphs in Figure 8, linear correlations are particularly good in the systems clay- $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ and clay- $\text{CaCO}_3\text{-NaCl-CO}_2\text{-H}_2\text{O}$ between sodium and pH. The linear correlation is questionable in the system clay- $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ when slope and sodium are compared. In no case is the correlation outstandingly good. The redundancy and scatter of data in the lower range of sodium concentrations and, at the same time, the few values of pH and slope available for use in this study at high sodium concentrations does not favor an accurate correlation analysis.

The results of the rank-method approximations for significant differences between systems in an attempt to establish the effects of lime, sodium chloride and gypsum on equilibrium pH and slope of the pH curve are summarized in Table 10. The hypothesis was made that the two systems being compared in each case were equal. If a significant difference was established, the hypothesis was rejected, as indicated by R in the table. If not, the result was indicated by F.R., meaning fail to reject.

Table 10.--SUMMARY OF RAPID APPROXIMATE STATISTICAL PROCEDURES TO DETERMINE THE EFFECTS OF CaCO_3 , NaCl AND GYPSUM IN CLAY SYSTEMS ON pH AND SLOPE OF THE pH CURVE

CLAY GROUP	¹ SYSTEM COMPARISONS					
	A:B	A:C	A:D	B:C	B:D	C:D
<u>Comparisons of pH at 0.0003 atm. CO_2</u>						
Bentonite---	² R(-)	R(-)	R(+)	F.R.	R(+)	R(+)
Fort Collins	R(-)	R(-)	F.R.	R(-)	R(+)	R(+)
57A-----	R(-)	R(-)	R(-)	F.R.	R(+)	R(+)
Kaolin-----	R(-)	R(-)	R(-)	R(-)	F.R.	R(+)
<u>Comparisons of slopes of pH curves</u>						
Bentonite---	R(+)	R(+)	R(+)	F.R.	R(+)	R(+)
Fort Collins	R(+)	F.R.	R(+)	R(-)	R(+)	R(+)
57A-----	F.R.	F.R.	R(+)	F.R.	R(+)	R(+)
Kaolin-----	R(+)	R(+)	R(+)	F.R.	R(+)	F.R.

¹System symbols represent the following:

- A Clay- CO_2 - H_2O
- B Clay- CaCO_3 - CO_2 - H_2O
- C Clay- CaCO_3 - NaCl - CO_2 - H_2O
- D Clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O

²Comparison symbol R means hypothesis that systems are equal in character was rejected by test. F.R. means hypothesis that systems were similar was not rejected. A negative sign (-) indicates that the first system is lower than the second in pH or slope value. A positive sign (+) indicates first system higher in value compared.

The following results for all clay systems with respect to pH at 0.0003 atmospheres CO_2 (equilibrium) were obtained, according to the comparisons in Table 10:

1. pH in the system clay- CO_2 - H_2O was lower than in the system clay- CaCO_3 - CO_2 - H_2O .
2. pH in the system clay- CO_2 - H_2O was lower than in the system clay- CaCO_3 - NaCl - CO_2 - H_2O .
3. pH in the system clay- CO_2 - H_2O was:
higher than in the gypsum system for bentonite;
not significantly different from the system Fort Collins clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O ;
lower than the pH of the system clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O in the case of 57A and kaolin clays.
4. pH in the system clay- CaCO_3 - CO_2 - H_2O was:
not significantly different from that of the clay- CaCO_3 - NaCl - CO_2 - H_2O system in the case of the bentonite or 57A clays;
lower than that of the clay- CaCO_3 - NaCl - CO_2 - H_2O system in the case of the Fort Collins and kaolin clays.
5. pH in the system clay- CaCO_3 - CO_2 - H_2O was:
greater than that of the clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O system in the case of all clays except kaolin, in which case no significant difference was established.
6. pH in the system clay- CaCO_3 - CO_2 - H_2O was greater than in any system containing gypsum, regardless of the type of clay.

The following results with respect to slope of the pH curve were obtained:

1. Slope in the system clay- CO_2 - H_2O was greater than in any systems which contained gypsum.
2. Slope in the system clay- CaCO_3 - CO_2 - H_2O was greater than in any systems containing gypsum except those of kaolin clays, in which cases the slope was greater when NaCl and gypsum were present.
3. Slope in the system clay- CO_2 - H_2O was greater than in those which contained CaCO_3 , except in the case of the 57A clay systems.
4. The system clay- CaCO_3 - NaCl - CO_2 - H_2O had a greater slope of pH curve than systems which contained, in addition, gypsum, except in the kaolin clay systems.

5. The system clay- CO_2 - H_2O had greater slope of pH curve than bentonite and kaolin systems which contained both CaCO_3 and NaCl , but did not differ significantly from Fort Collins and 57A clay systems which contained the two additional constituents.
6. Clay systems containing CaCO_3 alone had less slope of pH curve than those which contained in addition NaCl in the case of the Fort Collins clay systems only. No significant differences were established in the case of other clays.

Soil system studies

Some physical and chemical characteristics of the twelve Grand Junction Area soils were determined by rapid approximate procedures in the laboratory. The results are presented in Table 11. The range in soil texture was from sandy loam to clay. At saturation, the pastes of the soils contained from 27 to 49 percent water. The percentage of total soluble salts as determined by resistance measurements of the soil paste ranged from 0.12 to 3.0 or more. The conductivity in millimhos per centimeter of the saturation extracts of the soils varied from 2.6 to 33.3, the two extremes being represented by samples 5A and 57A respectively. By use of simple, empirical conversion methods given by the Regional Salinity Laboratory (62:47), these values were converted to represent a range of approximately 0.07 to 1.37 percent soluble salts in the soil, taking into consideration the degree of saturation of the soils with water. These values were a contrast to those obtained by the resistance measurements

Table 11.--SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF TWELVE GRAND JUNCTION AREA SOILS

SAMPLE	TEXTURE	SATURATED SOIL PASTE			SATURATION EXTRACT		SOL- UBLE Na %	EXCH. Na %	LIME % (CaCO ₃)	GYPSUM m.e.per 100 g. soil
		pH	H ₂ O %	Soluble salts %	Conductivity mmhos/cm.	Soluble salts %				
5A	Clay L.	7.78	37	0.14	2.60	0.07	18	2	16	0.90
6A	Loam	8.41	31	0.44	14.00	0.30	75	30	15	4.38
8A	Clay	8.47	37	2.36	28.20	0.83	99+	80+	21	4.51
13A	Loam	8.35	33	0.68	19.20	0.46	84	42	7	1.43
15C	Loam	8.96	34	1.22	28.20	0.77	99+	80+	16	10.96
16A	Sa.Lo.	8.21	27	0.12	4.32	0.08	62	14	7	0.10
23B	Si.C.L.	8.78	38	1.37	26.70	0.80	99+	79	15	12.14
26A	Clay L.	8.82	41	1.75	25.20	0.80	99+	79	18	11.53
29A	Loam	7.68	36	0.11	5.11	0.12	19	3	17	0.05
34B	Loam	7.82	38	0.28	9.07	0.23	57	15	9	8.65
45C	Clay	7.64	45	1.58	26.30	0.92	90	52	7	0.21
57A	Si.C.	7.38	49	3.00	33.30	1.37	71	35	9	0.11

of the soil pastes. Neither method can be considered especially accurate. The range in soluble sodium percentage was from 18 to more than 99, and the approximate exchangeable sodium percentages varied from 2 to more than 80. The percentage of lime in the soils, estimated by acid neutralization, was as low as 7 and as high as 21. Gypsum was present in amounts ranging from 0.05 to 12 milliequivalents per 100 grams of soil. Though the results presented in Table 11 must be considered approximate only, considering the methods of determination applied, they do furnish an indication of some of the more important properties and constituents of this group of soils, and provide an aid to the interpretation of pH behavior.

The permeability characteristics of the soils are illustrated in Figure 9. The coefficient of permeability in centimeters per hour was plotted against time in hours, commencing with the initial outflow of leachate from the base of the soil column. The maximum and final (13-day) permeability rates observed are recorded in Table 12. There is no permeability curve for soil 13A, and a very flat one for 45C. The former soil did not exhibit recordable permeability; the latter had a very low permeability rate. Several of the soils, including 6A, 8A, 15C and 34B, displayed somewhat good initial permeability rates, but became increasingly resistant to water movement, as did the remaining soils with time.

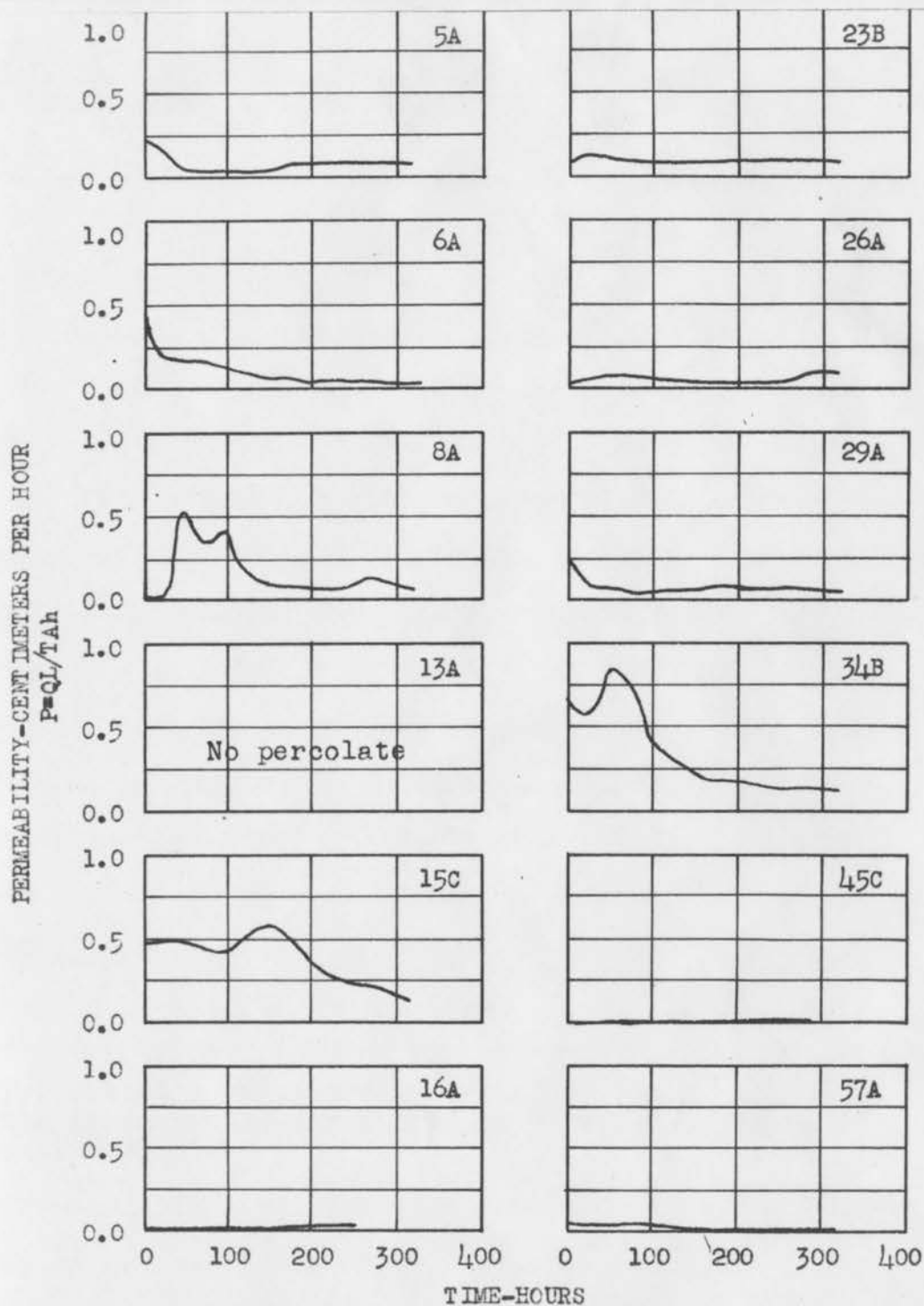


Fig. 9.--Permeability-time curves of twelve Grand Junction Area soils.

[Soils were leached with tap water at a constant temperature of 22°C.]

Table 12.--PERMEABILITY AND LEACHING RESULTS OF TWELVE
GRAND JUNCTION AREA SOILS

Soil	¹ Maximum perme- ability cm./hr.	² Final perme- ability cm./hr.	³ Initial soluble salts mgm/100g.	⁴ Soluble salts removed mgm/100g.
5A	0.097	0.068	140	440
6A	0.051	0.041	440	1120
8A	0.409	0.066	2360	2830
13A	0.000	0.000	680	400
15C	0.588	0.137	1220	3560
16A	0.043	0.043	120	185
23B	0.141	0.089	1370	3480
26A	0.094	0.094	1750	2920
29A	0.093	0.054	110	400
34B	0.084	0.120	280	1900
45C	<0.004	<0.004	1580	1330
57A	0.050	0.015	3000+	2210

¹Permeability value from point of presumed maximum on the permeability curve (Figure 9) after solution of entrapped air.

²Permeability after thirteen days of continuous leaching.

³Based on resistance of soil paste data, Table 11.

⁴Based on conductivity of composite leachate, and use of an average milliequivalent weight of 66.4(19:42-3).

Sample 8A displayed considerable initial resistance to water movement, accompanied by swelling and cracking, leading to channeling along the sides of the tube and accounting for false high permeability rates. Eventually the channels sealed and the rate of permeability approached a more representative value for that soil. Samples 15C and 34B sealed rapidly beyond the peak of maximum permeability, but they remained well above the others in final rate. By observation, they did not show the extreme breakdown of structure evident in the other soils. Three soils (13A, 16A and 45C) progressed very slowly with infiltration and salt removal. It was necessary to subject them to further leaching on Buchner funnels to bring the salt concentration of the leachates to comparative values with the other soils.

The approximate total amounts of soluble salts removed from the soils during the leaching process are also summarized in Table 12. For comparison, an estimate of the amounts of salts present before leaching is also given for each soil, based on data from Table 11. In some cases an excess of soluble salts was removed over the amount that was estimated to be present originally. This was probably due to the removal of such more slowly soluble compounds as gypsum.

All of the soils effervesced freely with dilute acid after leaching, indicating excess CaCO_3 in all.

The results of the pH determinations of the twelve Grand Junction Area soils are presented in Table F of Appendix B. The pH curves, based on the data, are presented in Figures 10 and 11. These are reductions of the original graphs, of the type shown in Figure B of Appendix B. Equilibrium pH values at 0.0003 and one atmosphere partial pressure of CO_2 were taken from the curves and are presented in Table 13. Also included in Table 13 are the initial pH values observed in the un-equilibrated suspensions of the soils, and the slopes of the pH curves. Grouped pH curves of the twelve soils are shown in Figures 6 and 12.

The following general statements applying to the soil studies are made on appraisal of the data and graphs:

1. The range in pH at low CO_2 equilibrium was 8.09 to 8.95 for the unleached samples, and 8.48 to 8.93 for the leached samples. These compare with a range in pH of 7.38 to 9.71 in the unequilibrated samples, including the soil pastes, 1 to 5 and 1 to 50 suspensions.
2. The changes in pH at low CO_2 pressure before and after leaching varied with the sample. Soils 6A, 23B, 29A, 34B, 45C and 57A showed an increase in pH. Soils 5A, 8A, 13A, 15C, 16A and 26A decreased in pH after leaching.
3. The range in slope values of the pH curves before leaching was 0.582 to 0.838. After leaching, the range was 0.668 to 0.790.
4. The changes in slopes of the pH curves varied with the samples. Soils 6A, 8A, 23B, 29A, 34B, 45C and 57A showed an increase in slope values. Soils 5A, 13A, 15C, 16A and 26A showed a decrease.
5. One apparent effect of leaching on the soils as a group was a narrowing of the range in both pH and slope values, as is apparent in Figure 12.

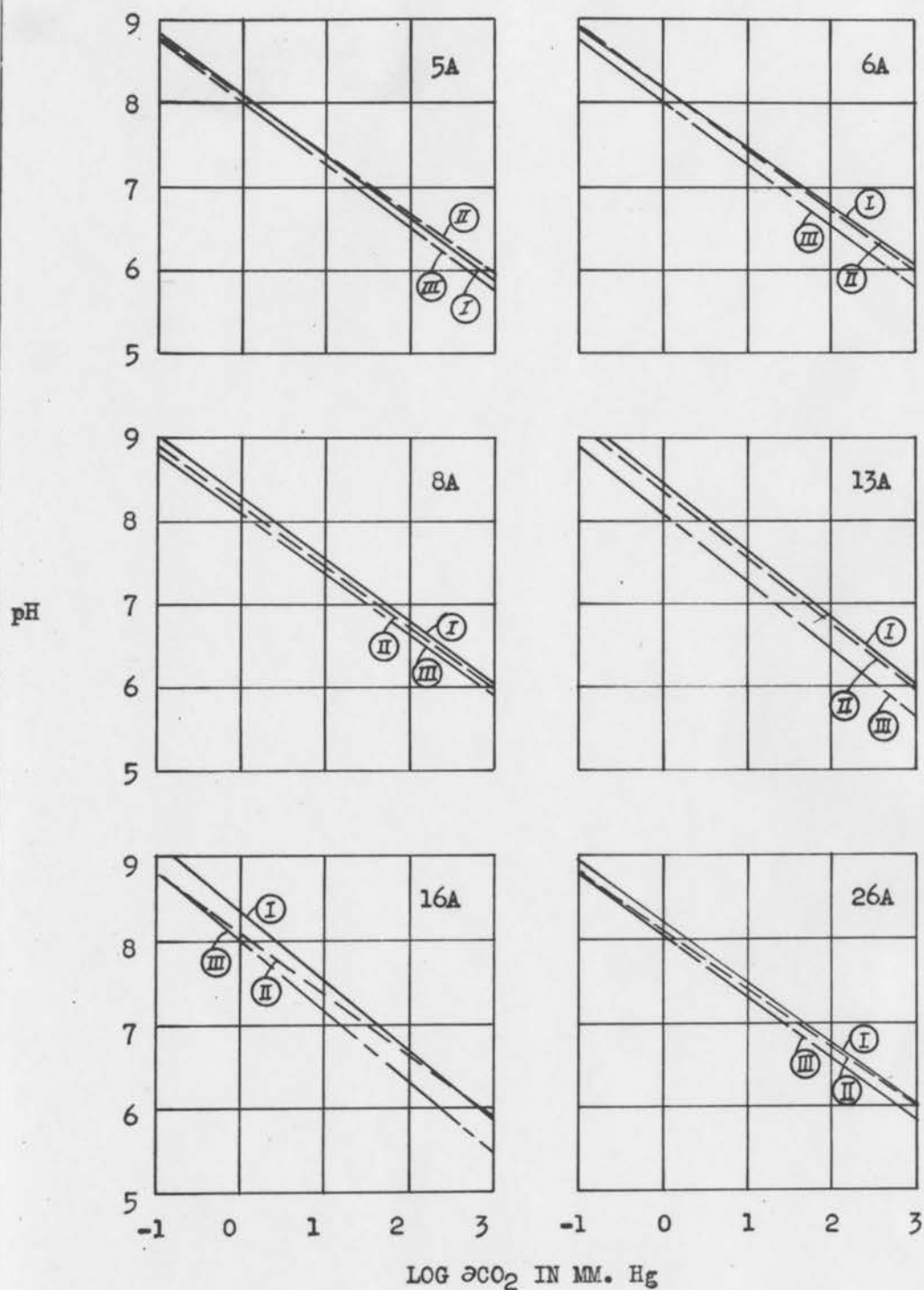


Fig. 10.--The pH curves of Grand Junction Area soils at 20°C.

[(I) before and (II) after leaching when the soil to water ratio was 1 to 5, and (III) before leaching when the soil to water ratio was 1 to 50]

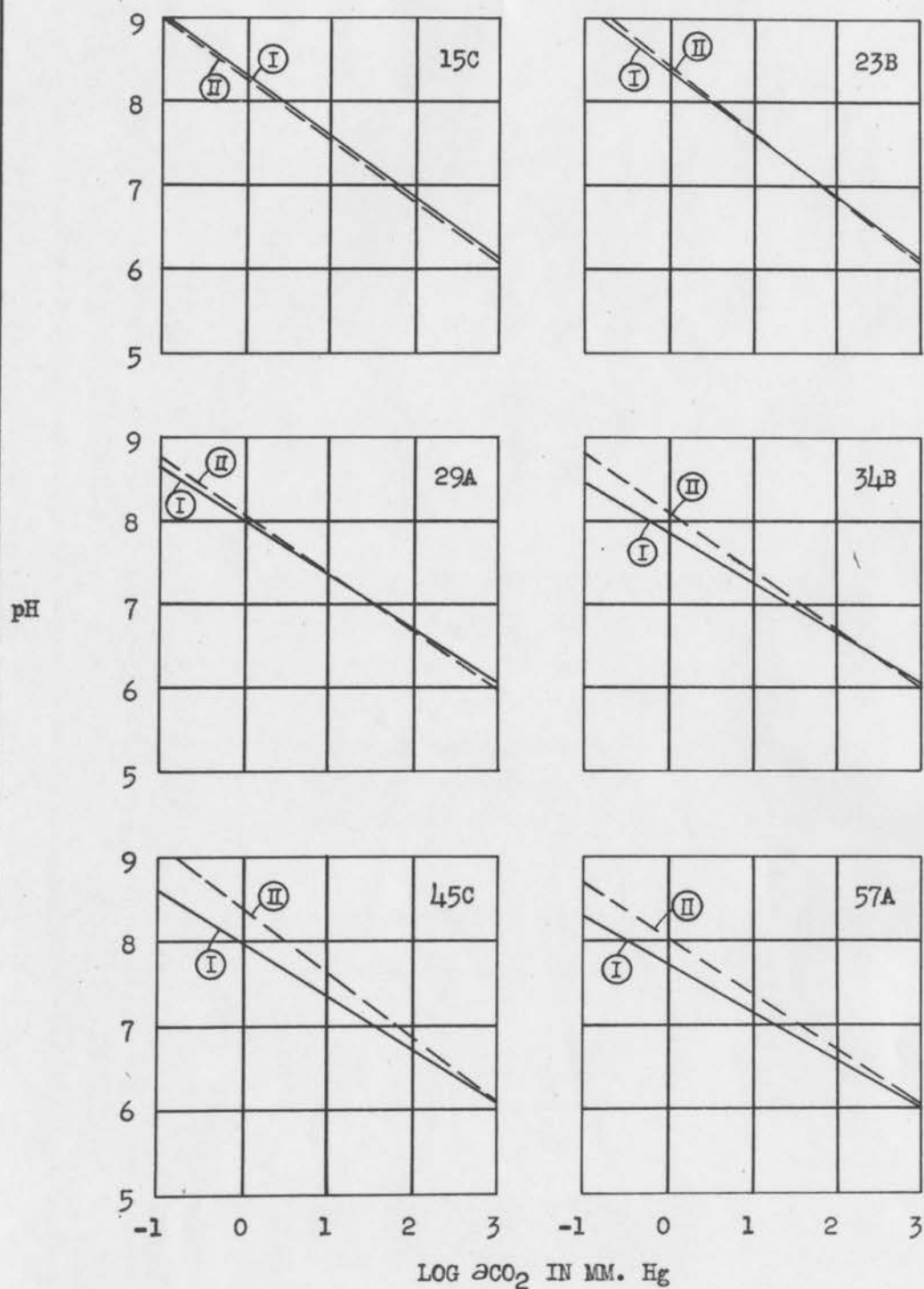


Fig. 11.--The pH curves of Grand Junction Area soils at 20°C.

[(I) before and (II) after leaching when the soil to water ratio was 1 to 5]

Table 13.--THE pH AND SLOPES OF THE pH CURVES OF TWELVE GRAND JUNCTION AREA SOILS

SAMPLE AND SOIL TO WATER RATIO	BEFORE LEACHING				AFTER LEACHING				Δb
	Initial pH	pH at 0.0003 atm. ∂CO_2	pH at 1 atm. ∂CO_2	l_b	Initial pH	pH at 0.0003 atm. ∂CO_2	pH at 1 atm. ∂CO_2	b	
5A:1 to 5	8.41	8.54	5.98	0.727	8.40	8.51	6.05	0.699	-0.028
1 to 50	9.02	8.47	5.86	0.741					
6A:1 to 5	8.89	8.60	6.17	0.690	8.68	8.63	6.06	0.730	0.040
1 to 50	9.31	8.47	5.89	0.733					
8A:1 to 5	9.15	8.72	6.17	0.724	8.71	8.64	6.05	0.736	0.012
1 to 50	9.40	8.53	5.97	0.727					
13A:1 to 5	9.59	8.95	6.12	0.804	9.66	8.86	6.08	0.790	-0.014
1 to 50	9.71	8.60	5.72	0.818					
16A:1 to 5	9.62	8.84	5.95	0.821	8.88	8.56	5.99	0.730	-0.091
1 to 50	9.43	8.53	5.58	0.838					
26A:1 to 5	9.31	8.68	6.12	0.727	8.80	8.55	6.06	0.707	-0.020
1 to 50	9.20	8.50	5.93	0.730					
15C:1 to 5	9.33	8.77	6.21	0.727	8.98	8.70	6.15	0.724	-0.003
23B:1 to 5	9.39	8.83	6.20	0.747	8.92	8.93	6.17	0.784	0.037
29A:1 to 5	8.56	8.40	6.12	0.648	8.62	8.50	6.07	0.690	0.042
34B:1 to 5	8.40	8.26	6.12	0.608	8.65	8.55	6.07	0.705	0.097
45C:1 to 5	8.45	8.38	6.16	0.631	9.31	8.88	6.20	0.761	0.130
57A:1 to 5	7.99	8.09	6.04	0.582	8.46	8.48	6.13	0.668	0.086

$l_b = \Delta\text{pH} / \Delta\log \partial\text{CO}_2$ is the slope of the pH curve, a negative value in every case.

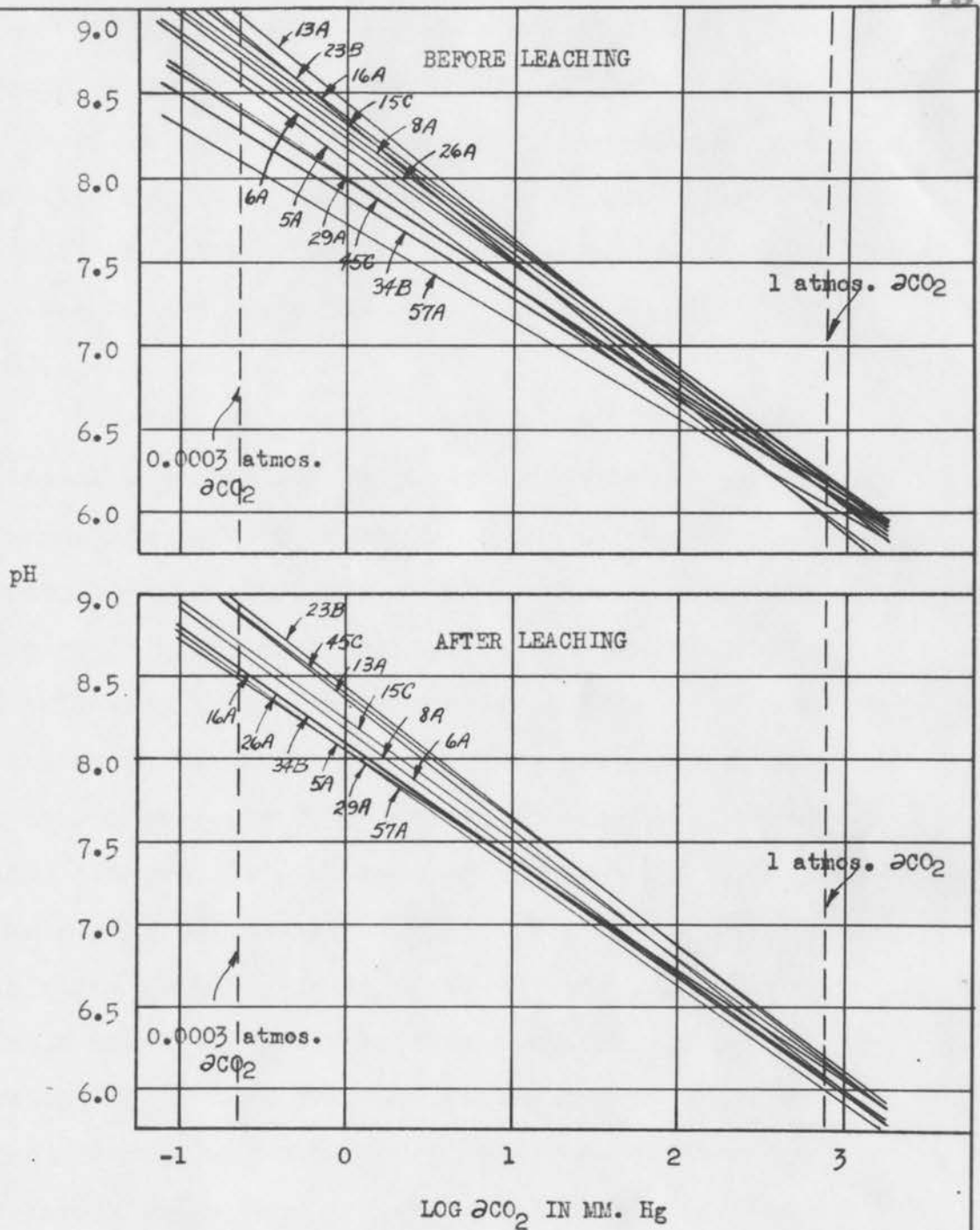


Fig. 12.--Grouped pH curves of twelve Grand Junction Area soils at 20°C.

[The soil to water ratio was 1 to 5. The soil sample number is indicated]

The mean pH of the 24 equilibrium pH values of all samples before and after leaching (soil to water ratio of 1 to 5) at 0.0003 atmospheres CO_2 partial pressure was 8.62 ± 0.04 , and the standard error of a single observation was ± 0.21 pH unit. These statistics were computed by the small sample methods recommended by Leonard and Clark (29:62).

A concept of pH changes due to CO_2 pressure variations was obtained by plotting pH values against the corresponding partial pressure of CO_2 at equilibrium. The results obtained for four of the soils are presented in Figure 13. The data for the curves were obtained from enlargements of the pH curves in Figures 10 and 11. The change in pH in the range of CO_2 pressures below 0.02 atmospheres was rapid, as noted also in the clay systems (Figure 7). The rate of change of pH diminished at the higher CO_2 pressures. The pH range of the four soils which probably could occur at 1 to 5 soil to water ratio in the field would be from about pH 7.5 to 6.5, assuming CO_2 partial pressure variations in the field ranged between 0.02 and 0.2 atmospheres. The data of many investigators would seem to indicate such a pressure range might be generally expected (9, 38, 49).

The effect of dilution was studied by determining the pH of suspensions of six of the soils at a dilution ratio of 1 part soil to 50 parts water. The

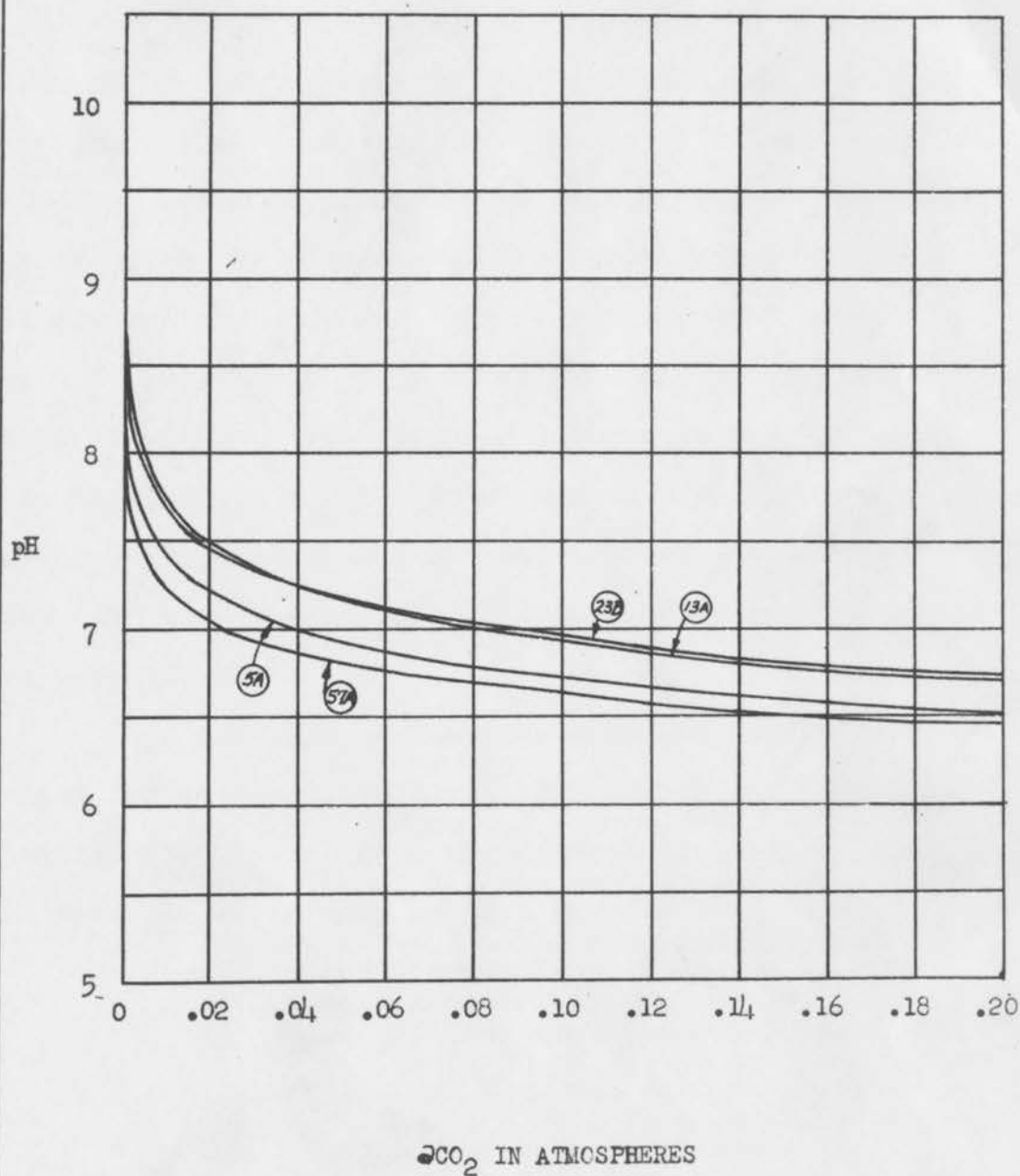


Fig. 13.--Effect of increasing CO₂ pressure on the pH of soil suspensions.

[The soil to water ratio was 1 to 5. The data were obtained from the pH curves of the soils. See Fig. 10 and 11]

purpose was to determine if extreme variations would occur, in order to properly evaluate the results of the clay system studies with those of the soil studies. The data was given in Table 13, the equilibrium pH values at 0.0003 and one atmosphere CO_2 partial pressure having been obtained from the pH curves, Figure 10. The pH of the soil suspensions having a 1 to 50 dilution ratio varied from 0.07 to 0.35 pH units lower than the pH of the 1 to 5 dilutions. In every case of the six studied, dilution resulted in a lower pH at constant CO_2 pressure. Likewise, slope values of the pH curves increased in every case with increasing dilution, though some increases were very slight.

An analysis of the data gathered in the soil studies for each soil follows. All pH values given refer to equilibrium with 0.0003 atmospheres CO_2 partial pressure.

Soil 5A is a highly calcareous clay loam, low in soluble salts, low in exchangeable sodium and gypsum. Permeability, though low, does not drop appreciably with continuous leaching. The pH of 8.54 changes little with leaching to 8.51. The slope of the pH curve decreased significantly. The soil system appeared to be predominantly of the Ca-clay- CaCO_3 - CO_2 - H_2O type, both before and after leaching.

Soil 6A is a highly calcareous loam, containing moderate amounts of soluble salts, appreciable sodium and moderate gypsum concentrations. The permeability diminished from an initial moderate to a low value during leaching. The pH increased slightly from 8.60 to 8.63 when the soluble salts were removed; the slope of the pH curve increased significantly after leaching. The system seemed to be of the type Na-Ca-clay- CaCO_3 -NaX- CaSO_4 - CO_2 - H_2O

- before leaching, changing probably to one of the type Ca-clay- $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ after leaching. (NaX represents various Na salts).
- Soil 8A is a very highly calcareous clay, also high in soluble salt content and sodium, but with only moderate gypsum content. The permeability was initially rapid, but the soil sealed quickly and permeability became very low. The pH dropped due to leaching from 8.72 to 8.64. The slope of the pH curve increased slightly. The soil system before leaching appeared to be of the type Na-clay- $\text{CaCO}_3\text{-NaX-CaSO}_4\text{-CO}_2\text{-H}_2\text{O}$. After leaching, the data indicated some change towards a system of the type Na-Ca-clay- $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$.
- Soil 13A is a moderately calcareous loam, moderately high in soluble salts and sodium. The gypsum content is moderately low. The sample had no permeability; leaching was forced on a Buchner funnel. Removal of soluble salts was not too complete. The pH before leaching was 8.95; this was the highest value of any of the soils. After leaching, the pH dropped to 8.86. The slope of the pH curve decreased slightly due to leaching, but still remained about 0.8, a high value in comparison to other soils. The system indicated before leaching was of the type Na-Ca-clay- $\text{CaCO}_3\text{-NaX-CO}_2\text{-H}_2\text{O}$, and seemed to change but slightly to one of lower sodium content.
- Soil 15C is a highly calcareous loam, high also in soluble salts, sodium and gypsum. The permeability of the soil was comparatively high, and remained fairly good even with some decrease over the thirteen-day period. The pH dropped from 8.77 to 8.70 with leaching. The slope of the pH curve decreased very slightly. The soil appeared to be a complex Na-Ca-clay- $\text{CaCO}_3\text{-NaX-CaSO}_4\text{-CO}_2\text{-H}_2\text{O}$ system before leaching, changing more to a Ca-clay- $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system after leaching.
- Soil 16A is a moderately calcareous sandy loam, low in soluble salts and gypsum, but containing some sodium. The permeability was markedly low from the start, but increased slightly with time. The pH dropped appreciably from 8.84 to 8.56 due to leaching. The slope of the pH curve changed from 0.821 to 0.730, a marked decrease due to leaching. It was apparent the soil system probably changed from a Ca-Na-clay- $\text{CaCO}_3\text{-NaX-CO}_2\text{-H}_2\text{O}$ complex

- to a system of the type $\text{Ca-clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$.
- Soil 23B is a highly calcareous silty clay loam, high in soluble salts, sodium, and gypsum. The permeability was moderately good by comparison and did not change significantly with time. The pH increased from 8.83 to 8.93, and the slope of the pH curve from 0.747 to 0.784. The system appears to have changed but slightly from one of a complex type: $\text{Na-Ca-clay-CaCO}_3\text{-NaX-CaSO}_4\text{-CO}_2\text{-H}_2\text{O}$.
- Soil 26A is a highly calcareous clay loam, high in soluble salts, sodium and gypsum. The permeability was somewhat low, but did not change appreciably with leaching. In fact, a slight increase seemed to occur. The pH dropped from 8.68 to 8.55, and the slope of the curve decreased from 0.727 to 0.707. The system, as complex originally as that of 23B, seemed to change to one more of the type $\text{Ca-clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$.
- Soil 29A is a highly calcareous loam, low in soluble salts, sodium and gypsum. The permeability was moderate and did not change too appreciably with time. The pH increased from 8.40 to 8.50, and slope of the pH curve increased from 0.648 to 0.690. These changes did not appear too significant. The system was predominantly of the $\text{Ca-clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ type both before and after leaching.
- Soil 34B is a moderately calcareous loam, of moderate soluble salt and gypsum content, but somewhat low in sodium. The permeability was very good in comparison to the other soils, but dropped sharply with time, remaining, however, at a moderately good rate. The pH increased from 8.26 to 8.55, and slope of the pH curve increased from 0.608 to 0.705. The system appears to have changed from one of the $\text{Ca-clay-CaCO}_3\text{-NaX-CaSO}_4\text{-CO}_2\text{-H}_2\text{O}$ type to the $\text{Ca-clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ type.
- Soil 45C is a moderately calcareous clay, high in soluble salts, moderate in sodium, and low in gypsum. The permeability was very low, and the soil had to be force-leached on a Buchner funnel. The pH increased from 8.38 to 8.88, and slope of the curve from 0.631 to 0.761, the largest slope change of any soil. The system seemed to change from a $\text{Ca-Na-clay-CaSO}_4\text{-CaCO}_3\text{-NaX-CO}_2\text{-H}_2\text{O}$ complex to one of the $\text{Ca-Na-clay-CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ type.

Soil 57A is a moderately calcareous silty clay, very high in soluble salts, but of moderate sodium and low gypsum content. The permeability was low and decreased with time. The pH increased from 8.09, the lowest value of the twelve soils, to 8.48. The slope of the pH curve increased markedly from 0.582 to 0.668. The system seems to have changed from one of the type Na-Ca-clay- CaCO_3 -NaX- CaSO_4 - CO_2 - H_2O to the type Ca-clay- CaCO_3 - CO_2 - H_2O .

Thus, the data of the soils studies has been summarized, with the reminder that observations are comparative both between soils and between soil systems and clay systems. The effects of dilution would indicate that higher pH values may logically occur in the soil systems due to the lower dilution.

Summary

In summary of the data of all studies conducted, the following significant observations are cited:

1. The time necessary to attain an equilibrium between air- CO_2 mixtures and soil suspensions having a soil to water ratio of 1 to 5 was within 48 hours when the partial pressure of CO_2 was less than about 0.006 atmospheres, but within several hours at higher CO_2 pressures.
2. Equilibrium pH at 0.0003 atmospheres CO_2 was significantly higher in bentonite, Fort Collins and 57A clay systems than in kaolin clay systems, but not significantly different between bentonite and Fort Collins clays, or between bentonite and 57A clays. The pH of the Fort Collins clays was higher than that of the 57A clays.
3. The slopes of the pH curves of the bentonite and Fort Collins clay systems were significantly greater than those of the 57A soil-clay and kaolin clay systems. The bentonite and Fort Collins did not differ significantly from one another. Likewise, the 57A and kaolin clays did not show significant differences in slope.

4. Significant correlations existed between the milliequivalents of sodium present per 100 grams of clay in the systems and pH at 0.0003 atmospheres CO_2 equilibrium as well as between sodium and slope of the pH curve in systems of the following types: clay- CO_2 - H_2O , clay- CaCO_3 - CO_2 - H_2O , and clay- CaCO_3 - NaCl - CO_2 - H_2O . No significant correlation with respect to these factors was noted in the system clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O .
5. The effects of calcium carbonate added to any clay- CO_2 - H_2O system were marked in increasing pH at low partial pressures of CO_2 . Calcium carbonate caused a decrease in the slopes of the pH curves, except in 57A clay systems.
6. The effects of sodium chloride on pH and slope of the pH curve varied with the clays. An increase in pH occurred in the Fort Collins and kaolin clay systems. No change occurred in the bentonite and 57A clay systems. Slope values increased only in the Fort Collins clay systems, but did not change significantly, if at all, in the others.
7. The effects of gypsum were to lower the pH in all clay- CaCO_3 - NaCl - CO_2 - H_2O systems, and to decrease the slope of the pH curves of all but the kaolin systems of this type. Gypsum-containing systems were also lower in pH than most other systems of all types, with a few exceptions. Likewise, gypsum systems had lower slope values than most other systems.
8. Twelve Grand Junction Area soils in suspensions having a soil to water ratio of 1 to 5 and at equilibrium with 0.0003 atmospheres CO_2 had a pH range of 8.09 to 8.95 before leaching, and 8.48 to 8.93 after leaching. The slopes of the pH curves ranged from 0.582 to 0.838 before leaching, and 0.668 to 0.790 after leaching. Changes in either pH or slope due to leaching were not consistent and varied with the samples.
9. All the soils were essentially clay- CaCO_3 - CO_2 - H_2O systems, with additional constituents such as soluble sodium compounds and gypsum probably accounting for the differences observed.
10. One outstanding effect of leaching the soils was a closer grouping of pH and slope of pH curve values, due probably to closer approach of all the systems to the Ca-clay- CaCO_3 - CO_2 - H_2O type as soluble constituents were removed.

Chapter V

DISCUSSION

The influence of carbon dioxide on soil reaction, or pH, was established by numerous investigators prior to this study. A considerable amount of research was also reported concerning the effects of various other factors on soil pH in a wide variety of soils and under diversified conditions. However, consideration and control of the carbon dioxide variable was largely neglected, in complete contradiction to natural field conditions under which CO_2 is a common constituent of the soil system (1, 9, 21, 30, 49, 60, 61). Concepts and interpretation of soil pH values determined in such manner have been subject to considerable question, particularly in the case of calcareous soils. The influence of CO_2 in soils containing an excess of calcium carbonate is pronounced (10, 34, 47, 63). The general use of pH as an index of soil properties is not without appreciable misinterpretation, doubt and error.

It was a purpose of this study to fully consider the CO_2 variable in pH determinations by establishing equilibrium in various clay and soil systems with known, constant, partial pressures of CO_2 , so that pH could be

expressed as a function of CO_2 pressure. The effects of other factors on pH were, therefore, more readily identified when the CO_2 pressure was held constant and known. The variability of pH at known, constant, partial pressures of CO_2 due to such factors as type of clay, sodium, calcium carbonate, sodium chloride and gypsum was studied in 96 carefully prepared clay systems. In this way, a fundamental approach to an understanding of CO_2 equilibria in soils was made. The data and concepts derived from these studies were applied to the interpretation of similar CO_2 equilibria studies of soil systems. Particularly, the usefulness of soil pH as a criterion of such factors as type of clay, sodium, calcium carbonate, sodium chloride, gypsum and permeability was investigated in twelve calcareous soils.

Type of clay mineral

Four distinct clay types were studied at equilibrium with known, constant partial pressures of CO_2 . Two represented pure samples of the clay minerals bentonite and kaolin. The others were clay separates of two Colorado soils. In a recent research study by Scott (51) in 1949, the presence of montmorillonite and illite was indicated in varying proportions in the clay separates of the two soils, with the possible inclusion of kaolin in soil 57A. Unfortunately, lack of time and

materials precluded the study of illite clay systems. The base exchange data obtained in this study is in general agreement with that of Scott.

The influence of the variability in type and predominance of specific clay minerals in the four clay groups prepared in this study with respect to pH could be examined from any number of viewpoints. Comparison of mean pH values at low partial pressures of CO_2 was chosen not only for maximum differences, but also in keeping with lowest CO_2 pressures and maximum pH values generally to be expected in soils under natural conditions. As a result of these comparisons, statistically highly significant differences were not obtained between the bentonite, Fort Collins and 57A (a Grand Junction Area soil) clay systems, the mean pH values at 0.0003 atmospheres CO_2 being respectively 8.37 ± 0.04 , 8.46 ± 0.06 and 8.28 ± 0.06 . The kaolin clays were significantly lower in pH than the three other groups, averaging 8.09 ± 0.04 .

The limited data and small samples upon which the statistical analysis was based do not afford especially dependable inferences from the results. There are indications, however, that the pH range in soils predominantly of montmorillonitic and illitic clays could be higher than that of soils which are largely composed of kaolinitic materials, but similar in all other respects. The magnitude of such differences is small in comparison to that

which may occur in any one soil when the CO_2 pressure changes from 0.0003 to 0.1 atmosphere. Differences due to clay minerals may not exceed 0.5 pH unit, and may be considerably less. A CO_2 pressure change from 0.0003 to 0.1 atmosphere can cause a pH change of 2.0 pH units or more.

The rate of change of pH with changing CO_2 pressure appears to vary with the type of clay mineral, as indicated by the mean slope differences of the pH curves. The bentonite and Fort Collins clay groups are closely related with respect to slope of pH curve, having mean values of 0.800 ± 0.016 and 0.798 ± 0.015 respectively. The 57A and kaolin clays were significantly lower in mean slope, having respective slope values of 0.743 ± 0.010 and 0.714 ± 0.013 .

Effect of sodium on pH

The effects of sodium on pH and characteristics of the pH curves of the clays were apparent in several ways. A trend, though not without exceptions, was noted towards a higher pH at low partial pressures of CO_2 in the clay suspensions, with or without the presence of calcium carbonate. The notable exceptions were the kaolin clays, and all systems containing gypsum. A statistical analysis for correlation between sodium and pH in different clay systems provided some significant

correlations in all cases but those systems which contained gypsum. This relationship of increasing sodium to increasing pH is in agreement with previous research (22, 32, 33). Critical study of the correlation graphs in Figure 8 brings to focus a noticeable lack of correlation between sodium and pH when the concentration of sodium is low. This is in agreement with the data of McGeorge (33) which indicated that pH is a function of replaceable sodium in soils of high exchange capacity when sodium is present in sufficient amounts to dominate the system. In soils with an exchange capacity below 10 milliequivalents, McGeorge was unable to identify any single dominating factor, as exemplified by the kaolin clays in this study. The lack of correlation of sodium with pH at known, constant, partial pressures of CO_2 noted by Puri and Uppal (46) might also be explained on this basis, as well as similar lack of correlation of pH with sodium found in Regional Salinity Laboratory studies (19).

Significant correlations between sodium and the slopes of the pH curves were also obtained. The higher sodium concentrations were associated with steeper pH-curve slopes. Again the kaolin systems and all others containing gypsum did not exhibit this relationship. The correlation was likewise obscured at low concentrations of sodium.

The importance of sodium as a factor affecting pH at CO_2 equilibrium is apparently dependent upon the amount of this constituent present in the system as well as the dominance of modifying effects of other constituents, such as gypsum. Wilson and his associates (31, 65) showed that the pH of the system $\text{NaHCO}_3\text{-CO}_2\text{-H}_2\text{O}$ varies directly with the sodium normality. The range of sodium normality, assuming all exchangeable sodium of the clays to pass into solution, was calculated to vary from 0.00005 to nearly 0.02 (not considering the sodium chloride added) in those systems which showed some correlation of sodium and pH. In the kaolin systems, the sodium normality range was from 0.00002 to 0.00083, thus overlapping that of the other clays and leaving some doubt as to the apparent lack of correlation between pH and sodium in the kaolin systems. Further study of the data in Table 6 discloses that the maximum differences in pH apparently due to sodium are 0.5 to 0.7 pH unit, comparing high and low sodium clays. The differences in slopes of the pH curves (Table 7) which can be linked to sodium variations range from 0.1 to nearly 0.2 slope units. These observations tend to support previous sodium hypotheses, inasmuch as the differences due to sodium are appreciable.

Effect of calcium carbonate on pH

Calcium carbonate had one outstanding effect in

all clay systems: the pH at 0.0003 atmospheres CO_2 partial pressure was increased by its addition. The pH increases were generally more pronounced in the systems of higher sodium concentration. These observations are in agreement with those of McGeorge (32,33), Gardner (22) and others who have related the higher pH of sodium-saturated, calcareous soils to the hydrolysis of carbonates. The evidence seems to bear out the concept that much sodium is brought into solution by calcium replacing sodium in the colloidal complex, thus also increasing pH.

Another important effect attributable to the addition of calcium carbonate in the system clay- CO_2 - H_2O was a definite, though slight, lessening of the slopes of the pH curves. This indicated that the hydrogen-ion concentration of systems containing calcium carbonate and at equilibrium with the higher partial pressures of CO_2 was more effectively reduced than the concentration at lower CO_2 pressures. In other words, the increase in pH due to the addition of lime was greater at the higher CO_2 pressures. The change in slope of the pH curves was indicative of the additional buffering caused by the $\text{Ca}(\text{HCO}_3)_2$ - H_2CO_3 pair.

A comparison of the clay- CaCO_3 - CO_2 - H_2O systems with the CaCO_3 - CO_2 - H_2O system in this study disclosed that the latter system has a lower pH at 0.0003 atmospheres CO_2 pressure than any of the clay systems except kaolin.

The slope of the pH curve of the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system was only 0.602; this was a significantly lower value than was determined for any of the 96 clay systems. Conversely then, clays sufficiently saturated with respect to bases will raise the pH of a calcareous system. This observation is in partial agreement with that of Simmons (54), who observed that a base unsaturated clay will accomplish this effect. The kaolin clays in this study most nearly approach that condition, but show little, if any, significant increase in pH over that of the pure CaCO_3 system.

The magnitude of the increase in pH due to calcium carbonate in systems of the type studied here ranged from 0.05 pH unit to more than one pH unit, the larger changes occurring at the higher CO_2 pressures. The slopes of the pH curves were reduced by as much as 0.1 slope unit, the most pronounced effects occurring in the bentonite and kaolin systems.

Effect of sodium chloride on pH

The effect of sodium chloride on the pH of clay systems at equilibrium with known, constant partial pressures of CO_2 was not uniform. Addition of the salt had no noticeable effect in the bentonite and 57A clay systems which also contained calcium carbonate. Sodium chloride increased the pH of Fort Collins clay and kaolin clay systems. The pH of all systems containing calcium

carbonate and sodium chloride together was significantly higher than those of the same systems without these added constituents, or with gypsum in addition. These results are in contrast to those of McGeorge (32) and Puri and Asghar (45) who observed that salts lowered the pH of soils which had not been equilibrated with known, constant partial pressures of CO_2 . The discrepancies between the data obtained in this study and that of other investigators are difficult to ferret out, considering the wide variety of methods and materials employed. If concentration of sodium chloride used in the various studies is compared, it is noted that generally higher concentrations were used in the other studies. The effect of sodium chloride has been shown by Frear and Johnston (20) to increase the solubility of calcium carbonate. If an excess amount of calcium carbonate is present, as in these studies, the bicarbonate ion concentration is increased. At constant CO_2 pressure, the chemical equilibrium established would include a lowering of the hydrogen-ion concentration. The pH would then rise, as was the case with respect to the Fort Collins and kaolin clay systems. The additional reactions which may occur, such as decomposition of the clay minerals, are beyond the scope of this report to consider. The extent of the data obtained in this study does not warrant more definite statements relative to sodium chloride effects on the pH of clay systems.

The effect of sodium chloride on the slopes of the pH curves is directly linked with the changes in pH caused by the addition of the compound, its effect on the solubility of calcium carbonate and resulting chemical reactions. Why sodium chloride would effectively change the slope of the pH curves of one group of clays--the Fort Collins--and not the others cannot be explained at this time. A considerable amount of additional data is needed to substantiate the effects noted in these studies.

Effect of gypsum on pH

The addition of an excess of gypsum produced a marked reduction in the pH of all systems of clays which contained both calcium carbonate and sodium chloride. Likewise, the slopes of the pH curves of the systems were significantly decreased, except in the case of the kaolin clay systems. The magnitude of the decrease in pH at 0.0003 atmosphere partial pressure of CO_2 equilibrium was about 0.5 pH unit, which agreed to some extent with the data of Bradfield (9), and of Shipley and McHaffie (52). Another marked effect of gypsum in the clay systems was a masking, or modification of the previous effects of sodium. Reeve and coworkers (48) suggested this effect in studies of soils in the field.

Again the data of Frear and Johnston (20) provide a possible explanation of gypsum effect at CO_2 equilibrium.

The addition of gypsum to a system of $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ decreases the solubility of the calcium carbonate, reducing the concentration of bicarbonate ions, and increasing the hydrogen-ion concentration in the establishment of a new equilibrium. This reaction appears to have occurred in the clay systems studied, the pH having been effectively reduced in all cases.

Carbon dioxide equilibria in soils

There are several general remarks which apply to any CO_2 equilibria studies conducted with a group of calcareous soils of this nature. Equilibration of suspensions of the soils proceeded at a rate which depended upon the partial pressure of the CO_2 , the concentration of the suspension, the concentration of calcium carbonate and soluble salts in the soils, and the efficiency of the equilibration apparatus. At CO_2 pressures below 0.0006 atmospheres, equilibration results for pH determinations were not satisfactory and erroneous data was often obtained. Considerable time was spent following an equilibration, yet results obtained one time did not agree within 0.2 pH unit of those later obtained. At CO_2 pressures between 0.0006 and 0.006 atmospheres, the time necessary to attain equilibrium between soil suspension and gas varied from 2 to 48 or more hours. Generally, in suspensions having a soil to water ratio of 1 to 5,

equilibrium was attained within 24 hours, and pH readings checking within 0.05 pH units were readily obtained. As the CO_2 partial pressure was increased, the time for equilibration in the suspensions decreased. At 0.06 atmospheres, equilibrium pH values were attained within twelve hours, and occasionally within six. Above 0.1 atmosphere partial pressure of CO_2 , the pH of the suspension was observed to make an initial rapid drop below the equilibrium value, then leveled off within two to six hours. The magnitude of the initial and final pH difference was seldom more than 0.07 pH unit. Equilibration proceeded more rapidly in suspensions having a soil to water ratio of 1 to 50. Additional important factors in obtaining reliable results included the maintenance of good line pressure to the bubblers, use of good gas-dispersion bubblers of uniform construction, and a supply of gas of as nearly constant CO_2 composition as possible throughout any one equilibration. Temperature control was observed, but changes of as much as 1°C did not noticeably affect pH results.

In agreement with the observation of Hoagland and Sharp (25), no permanent changes in soil reaction were noticed due to treatment with CO_2 . The pH of the soil suspensions readily changed with changing CO_2 pressure and were readily brought back to former values after various pressure changes.

The pH values of the twelve Grand Junction Area soils at known, constant, partial pressure of CO_2 , and the characteristics of the pH curves provided an indication of natural chemical equilibria which may occur in the soils. It appeared, however, that a considerable amount of additional research with soils and clays would be required to support the usefulness of pH at CO_2 equilibrium as a criterion of such soil properties as type of clay, sodium status, and permeability. In spite of the introductory nature of the equilibria studies, some interesting comparisons between the soils are possible. This group of soils, all from the same general area of Colorado, show widely divergent characteristics with respect to texture, pH as ordinarily determined, soluble salts, soluble and exchangeable sodium, and gypsum. The soils exhibited appreciable similarity in containing an excess of calcium carbonate in all cases. The base exchange capacity of the soils as a group ranges from about 10 to 15 milliequivalents per 100 grams of soil (51).

One of the first important considerations in appraising the soils was the pH range which might be expected under field conditions. An indication of this was provided by the equilibrium pH values at 0.0003 atmospheres and one atmosphere of CO_2 pressure. Soils 5A, 29A, 34B, 45C and 57A had a pH at 0.0003 atmosphere of less than 8.5, which dropped rapidly to a pH below 6.2 at

one atmosphere of CO_2 pressure. Only under a condition of sudden saturation, such as by flooding, might the higher pH values be expected in the field. Such conditions would probably be of too short duration and generally too distant from plant root-soil contact zones to exert any marked adverse influence on plant growth from a pH standpoint. A more likely range of pH under field conditions would be 7.5 to 6.5, as illustrated in Figure 13, which would be optimum with respect to many factors.

Considering that the remaining seven soils had pH values at equilibrium with 0.0003 atmosphere CO_2 partial pressure above 8.5 before leaching, the question of their suitability as mediums for plant growth is raised. But again, the range of pH in this group to be anticipated under field conditions would be about 7.75 to 6.75, only slightly more than the other soils and still within an optimum range for most plant and microbial growth.

The effect of leaching on the pH of the soils was not uniform, some increasing in pH after leaching by as much as 0.5 pH unit, and others decreasing nearly 0.3 pH unit. However, a significantly closer grouping of the soils in pH values and pH curve characteristics occurred, indicating, perhaps, that the removal of salts and changes effected in nature of base saturating the colloidal complex in the soils tended to reduce all to very similar systems. Since all the soil were high in calcium carbonate

content at the start, and all retained considerable amounts after leaching, it is probable these soils as a group most nearly represent the system Ca-clay-CaCO₃-CO₂-H₂O after leaching.

In comparing the characteristics of the soil systems with those of the clays as herein studied, it may be questioned that since the clay systems represented 1 to 50 dilutions and the soils were studied in 1 to 5 dilutions the results would not be comparable. The proportion of fine clay present in the clay suspensions, however, greatly exceeds that in the soil suspensions. The influence of clay should not be anticipated less in the higher-dilution clay suspensions for this reason. In fact, the clay influence in the clay systems would be exaggerated in comparison to its normal role in the average-textured-soil suspension.

In attempting to explain the apparent lack of correlation in the soils between the various factors of sodium percentages, soluble salts, permeability characteristics and pH at CO₂ equilibrium, an additional factor to be considered is the exchange capacity of the soils. The value is somewhat low, suggesting that in comparisons with clay systems, CO₂-equilibria phenomena in the soils might bear more similarity to those in the kaolin clay systems, rather than in other clays. Strikingly enough, the kaolin systems also showed inconsistencies in compari-

to other clays. The kaolin clays showed little, if any, significantly higher pH values than those of the pure calcium carbonate systems. It might, therefore, be suspected that the twelve Grand Junction Area soils have pH characteristics and variability due mainly to the soluble constituents and calcium carbonate, rather than to clay characteristics. The dominating influence in the soils seems to be calcium carbonate. Changes in pH due to leaching were reflections of the changes in the amounts and presence of modifying soluble salts, and closer approach of the soils to pure calcium carbonate systems. Bradfield (9) suggested that the pH values of soils which are predominantly calcareous systems would fall in the range 8.2 to 8.4 at CO_2 equilibrium under normal atmospheric conditions. The soils of this study varied in pH from 8.1 to 8.9, including results before and after leaching.

The pH changes which occurred in these soils indicated that such changes are complex when calcium carbonate, soluble salts and gypsum are present. A considerable amount of detailed study and analyses of soil suspensions at different stages of equilibria would be necessary to establish the reactions which occur. However, the experience of this study and the theory of the studies of Frear and Johnston (20), Hastings and Sendroy (23), Simmons (54) and Wilson and coworkers (65) indicate that,

fundamentally, the principal factor affecting pH changes at known CO_2 equilibria in these soils is the concentration of the bicarbonate ion as affected by changes in salt concentration and CO_2 pressure. The soils are predominantly $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ systems. The role of the clay appears significant but minor. The solubility of CaCO_3 and the resulting bicarbonate-ion concentration are functions of soluble salt concentrations and the partial pressure of carbon dioxide, and the pH variations are linked with these factors.

The recommendation of Whitney and Gardner (63) that an expression of the pH of soils as a variable function of the CO_2 pressure would give a better indication of the probable pH range in the field than single pH measurements is well illustrated in this study. The twelve Grand Junction Area soils, if judged on the basis of pH determined on soil pastes or in suspensions having a soil to water ratio of 1 to 5 when the partial pressure of CO_2 is variable and unknown, would be considered widely divergent with respect to pH suitability for crop growth. At known, constant partial pressures of CO_2 , the soils fall into a closer group with respect to pH characteristics and become more similar in this connection when leached. It would appear that the pH problem should be minimized in classifying the soils, and that such problems as types and amounts of salts, permeability and structure are of

much greater importance. However, the pH data obtained in the study provides a more accurate picture of the probable plant-root environment than pH ordinarily obtained. More detailed studies of this type might also provide a clearer concept of chemical equilibria in the soil, and pH-plant nutrient availability relationships.

A classification of the soils for reclamation development on the basis of equilibrium pH values or characteristics of the pH curves alone is not indicated in the light of the limited data thus far obtained. In fact, this procedure appears to be of less value in judging, for example, the probable sodium status of the soils than the method of pH changes with increasing dilution, ignoring CO_2 equilibration. However, the equilibria information, in conjunction with the results of rapid approximate analyses of the soils for soluble salt content, sodium, calcium carbonate and gypsum rectifies false conceptions of probable equilibria in the soils and facilitates a more reliable classification.

Suggestions for further study

The need for a considerable amount of data, particularly on soil systems, with respect to equilibrium pH values, slopes of pH curves and statistics based on the results is indicated. Clay studies are tedious and might present a somewhat distorted picture of soil

equilibria. However, they do provide fundamental concepts which can be applied with proper caution and interpretation to soil systems. Studies of such additional clays as illite are desirable. In addition to laboratory research, the need for soil atmosphere studies and CO_2 fluctuations in soils in situ is great. The existing data on CO_2 in soils is meager, local in importance and limited in application. A more significant method of studying CO_2 fluctuations in the soil than present gas well and gas sampling techniques might be developed by the determination of pH in the field and interpolation of CO_2 pressures from previously prepared pH "calibration" curves for the soil. Finally, the entire field of plant tolerances to pH should be reexamined in the light of equilibrium-pH concepts, as well as the relation of pH to nutrient availability and the solubility of inorganic soil supplements in calcareous soils. A greater amount of soil analyses and interpretation of results should be accomplished in cognizance of the CO_2 variable, its control, and its effect on soil pH. The phosphate problem in calcareous soils should be examined in full consideration of CO_2 equilibria relationships.

Chapter VI

SUMMARY

Carbon dioxide is a common constituent of soils and plays a dominant role in the control of chemical equilibria in the soil system. Previous research workers have demonstrated that soil reaction or pH is greatly influenced by the partial pressure of CO_2 in the soil system (46, 63). A considerable amount of data and theory has been accumulated stressing other factors affecting pH without consideration and control of the important CO_2 variable (2, 3, 7, 15, 32, 33, 45, 55). A resulting confusion of theory exists in the determination and interpretation of soil pH values, particularly for calcareous soils. This study, therefore, was undertaken to investigate the influence of some variables in the soil system on pH at constant, known, partial pressures of CO_2 , and the usefulness of pH thus determined in soil studies.

That chemical equilibrium in a soil suspension can be established by bubbling through it a gas of constant CO_2 composition or pressure has been demonstrated by a number of workers (10, 11, 46, 54, 63). An apparatus was assembled for this purpose, and a technique developed for the determination of pH in clay and soil suspensions

in equilibrium with known, constant, partial pressures of CO_2 .

Preliminary studies with suspensions of six Grand Junction Area soils disclosed rates of equilibration--that is, the time elapsed in subjecting soil suspensions to bubbling before constant, reproducible pH readings were obtained--varying from one to 48 hours, dependent upon the partial pressure of CO_2 in the air- CO_2 gas mixture, and the concentration and composition of the suspension. At partial pressures of CO_2 exceeding 0.1 atmosphere and in the more dilute suspensions equilibration was most rapid.

Groups of four separate clay materials were fractionated from raw bentonite, washed kaolin, the Fort Collins loam soil and a Grand Junction Area soil (57A), to limit particle sizes to those less than one micron in diameter. Supercentrifugation, sedimentation and flocculation techniques were employed. From each stock clay, six clay systems of varying sodium-calcium status were prepared by washing portions of the clays with one-normal chloride solutions of sodium and calcium, mixed in different ratios.

The clays, in groups of six, were next prepared in two-percent aqueous suspensions, analyzed, and equilibrated with four known, constant, partial pressures of CO_2 . Equilibrium pH values were obtained. The procedure was

repeated three more times as calcium carbonate, sodium chloride and gypsum were added in succession to form increasingly complex systems. The pH values of 96 separate clay systems were thus obtained. The data was analyzed statistically to determine the effects of type of clay, sodium, calcium carbonate, sodium chloride and gypsum on pH at CO_2 equilibrium. The slope of the pH curves was also calculated and subjected to statistical studies for significant differences.

Suspensions of twelve Grand Junction Area soils were equilibrated at four CO_2 pressure levels. The pH values were derived at 0.0003 atmospheres partial pressure of CO_2 for comparison with the clay-system data. Additional, rapid, approximate analyses for texture, soluble salt concentration, soluble and exchangeable sodium, calcium carbonate and gypsum were made. Samples of the soils were subjected to permeability and leaching studies. The pH of suspensions of the leached samples was determined and compared with the pH data of the unleached soils.

The kaolin clays were significantly lower in mean pH than the three other clay groups, averaging 8.09 ± 0.04 in contrast to 8.37 ± 0.04 for the bentonite clays, 8.46 ± 0.06 for the Fort Collins clays, and 8.28 ± 0.06 for the Grand Junction soil 57A clays. Differences due to clay minerals did not exceed 0.5 pH unit, and were generally considerably less.

The mean slopes of the pH curves of the bentonite and Fort Collins clay groups were closely related, being 0.800 ± 0.016 and 0.798 ± 0.015 respectively. The slopes of the pH curves of the 57A clay systems averaged 0.743 ± 0.010 ; those of the kaolin group averaged 0.714 ± 0.013 . These values were significantly less than the mean slope values of systems of the other two clays, but not significantly different from each other.

A trend toward higher pH at low partial pressure of CO_2 was noted with increasing sodium in all clay systems except those of kaolin or any containing gypsum in excess. Significant direct correlations between milliequivalents of sodium per 100 grams of clay and slopes of the pH curves were obtained with similar exceptions.

Calcium carbonate had one outstanding effect in all clay systems: the pH at low CO_2 partial pressure was increased by its addition. Also, the slopes of the pH curves were slightly decreased, but remained above the 0.602 value for the slope of the pH curve of the pure $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system.

Sodium chloride had no noticeable effect on pH in the bentonite and soil 57A clay systems, but did increase the pH in kaolin and Fort Collins clay systems. The slopes of the pH curves were increased in the Fort Collins clay systems, but not in the other clay systems.

The addition of an excess of gypsum produced a marked reduction of about 0.5 pH unit in all systems at 0.0003 atmospheres partial pressure of CO_2 . Likewise, the slopes of the pH curves were significantly decreased by gypsum, except in the kaolin clay systems.

The twelve Grand Junction Area soils varied widely in texture, sodium, gypsum and soluble salt status, but all contained excess free carbonates. The equilibrium pH values of the soils varied from 8.09 to 8.95 at 0.0003 atmospheres partial pressure of CO_2 . The effects of leaching were not uniform, and the range in pH values of the leached samples was 8.48 to 8.93. Some soils increased in pH due to leaching; others decreased in pH. The slope values of the pH curves varied from 0.582 to 0.838. The mean pH of all the soil systems was 8.62 ± 0.04 , and the mean slope of the pH curves was 0.715 ± 0.012 . All of the soils appeared to be clay- CaCO_3 - CO_2 - H_2O systems in general pH characteristics, both before and after leaching. Modifications and differences seemed to be due largely to the variability between the samples with respect to the amounts of soluble salts, gypsum and sodium present.

The effect of increasing the dilution of six soils from a 1 to 5 soil to water ratio to a 1 to 50 ratio was observed to be a significant lowering of pH at constant CO_2 pressure.

The technique of determining the pH of soils at equilibrium with known, constant, partial pressures of CO_2 provided a different concept of the soils than would generally be obtained by the usual methods of pH determination. It was observed that the pH of the Grand Junction Area soils under field conditions might normally range between 7.75 and 6.5, in spite of the fact that some of the soil contained considerable sodium. Classification of the soils for reclamation development on the basis of equilibrium pH values or characteristics of the pH curves alone was not warranted by the limited data thus far obtained. However, the information in conjunction with rapid, approximate analyses for significant soil constituents provided a distinct aid for the diagnosis of soil properties and capabilities for plant growth.

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APPENDIX A

OUTLINE OF METHODS

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I. Preparation of clays

A. Fractionation of samples

1. Preparation of suspensions

- a. Weigh out separate 2 mm.-sieved, 50-gram samples of the soil material. Add to stirring cup of Hamilton-Beach mixer, fill cup to within 2"-3" of top with tap water. Add 5 ml. 0.5 N NaOH and 5 ml. saturated $\text{Na}_2\text{C}_2\text{O}_4$, and stir for 15 to 30 minutes (one hour or longer for bentonite and similar materials).
- b. Decant suspension into glass jar, allow to settle for 5 minutes, then siphon suspension into 20-liter carboy half filled with tap water. Continue to add similarly prepared suspensions to carboy to create final volume of 15 liters of one percent suspension. The following approximate total weight of materials is required to prepare 15 liters:

Bentonite	160 grams
Fort Collins loam	400 grams
Kaolin	240 grams
Soil 57A	300 grams

- c. Place carboy on reciprocating shaker for 4 to 6 hours.

2. Separation of one micron fraction

(Either of the two following procedures were used).

a. Supercentrifugation (Sharples super-centrifuge).

1. Take duplicate 10 ml. aliquots of the 15 liters of suspension for percentage determination, and adjust suspensions to one percent if necessary and desired by further addition, dispersion and shaking.
2. Compute rate of flow through centrifuge cylinder and speed necessary to separate out particles greater than one micron size by use of formula: $t = 9ns/2r^2k_1f_0g(d_1-d_2)$, in which t is time for passage of unit volume (volume of cylinder) through centrifuge; n is viscosity of water in centipoises; s the maximum horizontal distance particles must settle to cylinder wall; r is radius of particles (assume spherical); k is percent suspension; f_0 a factor multiplying gravity and g the force of gravity, then f_0g is

the centrifugal force = $R\omega^2 = R(2\pi N)^2$ where N is revolutions per second; d_1 the density of the particles (g.cm^{-3}); and d_2 the density of the dispersion medium. The specifications of the centrifuge tube used follow:

Large diam. 4.45 cm. Length 20.1 cm. Vol. 312.57 cm^3 .
 Small diam. 2.54 cm. Vol. 101.85 cm^3 .
 Vol. of liquid to pass through was 210.7 cm^3 .

3. Adjust Mariotte siphon to carboy to provide approximate rate of flow desired through supercentrifuge. After bringing centrifuge up to speed, start flow through, checking rate of discharge by use of graduated cylinder and stopwatch and adjusting speed of centrifuge. After adjustment pass suspension through centrifuge into second carboy. Check speed of centrifuge and rate of discharge frequently, as described. Stop flow and centrifuge when not more than 5 liters of original suspension have passed

through, remove celluloid liner and replace with clean liner.

Proceed with separation until complete, agitating original suspension frequently.

4. To centrifuged suspension, add 0.5 N HCl to adjust pH to 5.0. Allow to stand 2 to 3 days then siphon off clear liquid carefully, reducing volume to approximately two liters. Shake and transfer to smaller container and repeat standing and siphoning to reduce volume to a minimum. In case of bentonite and similar clays, effective flocculation at pH 5.0 is not attained. Colloidal fraction is obtained by transfer of portions of suspension to large evaporating dishes on low hot plate and continuous evaporation almost to dryness.
5. Remove excess solution from flocculated clays by transfer of concentrated flocs to Buchner funnels.

b. Sedimentation

(this procedure was adopted owing to

greater convenience and adaptation to laboratory schedule).

1. Prepare approximately one percent suspensions as outlined previously (I.A.1).
2. After reciprocal shaking, allow to stand sufficient length of time for sedimentation of size fractions greater than one micron in diameter: $t = h/Cr^2$, in which t is time for sedimentation in seconds, h is depth of container, r the radius of particles in cm., and C a constant at given temperature. $C = (2/9)g(d_1-d_2)/\eta$, these factors being previously defined (I.A.2.a.2)
3. Transfer by siphoning carefully the suspension containing the size fraction less than one micron and proceed with flocculation and volume reduction as outlined (I.A.2.a.4).

B. Treatment with chloride solutions.

1. Preparation of chloride solutions.

- a. Prepare 1 N. solutions of NaCl and CaCl₂ (16 liters of each).

- b. Prepare volumetrically as needed wash solutions from the stock solutions as follows, or in such other ratios as may prove more satisfactory:

Ratio	ml. N NaCl	ml. N CaCl ₂
0Na-5Ca	0	1000
1Na-4Ca	200	800
2Na-3Ca	400	600
3Na-2Ca	600	400
4Na-1Ca	800	200
5Na-0Ca	1000	0

2. Washing treatment.

- a. To 60 grams of moist, one micron clay (from I.A.) add 500 ml. chloride solution in stirring cup of mixer. Stir for one to four hours (sufficient time to effect complete dispersion). Transfer to shaking bottle and allow to stand overnight.
- b. Siphon off as much of the clear solution as possible and transfer sample to Buchner funnel. Remove excess wash solution through Whatman No. 40 filter.
- c. Transfer sample to stirring cup, add 500 ml. of chloride solution and stir for one hour. Repeat Buchner funnel leaching and again stir with 500 ml. chloride solution to make total of 1500 ml. used in three washings. Drain.

- d. Transfer sample to stirring cup, add 500 ml. 95 percent ethanol and stir for one hour. Leach on Buchner funnel and repeat ethanol washing procedure (8 to 12 times) until specific resistance of leachate passes above 200,000 ohms. Use conductivity bridge and cell for test.
- e. Transfer sample to clean glass-stoppered jar preparatory to use.

II. Preparation of suspensions.

- A. Weigh out 6 to 8 grams of the moist, treated clay, transfer to 250-ml. wide-mouthed bottle and add 200 ml. distilled water. Stir until dispersion is complete (1 to 4 hours).
- B. Transfer suspension to clean shaker bottle. Pipette 10 ml. and transfer to clean, tared aluminum pan. Shake before each sampling.
- C. Oven dry at 110°C . for at least 24 hours. Remove to desiccator for cooling, weigh and compute percent suspension on weight basis.
- D. Adjust suspension to two percent point by addition of distilled water and stirring as needed. Store suspensions in stoppered shaking bottles marking original volume for reference.

III. Exchange capacity and exchangeable cation determination.

A. General procedure.

1. Transfer 10 ml. aliquot (or more, depending upon base saturation and capacity of clay) of suspension by pipetting to 50-ml. round-bottom, narrow-neck centrifuge tube. Add 20 ml. of 1 N. neutral ammonium acetate (57 ml. glacial acetic acid and 68 ml. conc. NH_4OH diluted to 1 liter and adjusted to pH 7.0). Stir until completely dispersed, rinse off stirrer with 10 ml. acetate solution and allow to stand overnight.
2. Centrifuge at 800 to 1200 rpm for 5 to 15 minutes (depending on clay). By use of hooked rubber-tipped glass rod, free adhering particles from neck of bottle, rinse with acetate solution and recentrifuge if necessary.
3. Decant clear liquid through 7 cm. No. 40 Whatman filter paper, catching filtrate in clean 250-ml. flask. Add 20 ml. 1 N neutral ammonium acetate, stir for 5 to 10 minutes, rinse stirrer off with 5 or 10 ml. acetate, centrifuge, and decant through same filter. Repeat ammonium acetate washing three more times for total of 150 ml. extract in flask.

Transfer extract to a 250-ml. beaker quantitatively, using small portions of distilled water to rinse flask into beaker.

4. Evaporate the extract to dryness (run blank of 140 ml. ammonium acetate and distilled water in volume used). Stir residue with stream of water and re-evaporate, repeating this process until free of ammonium acetate decomposition products.
5. Add 5 ml. distilled water to residue, then 3 ml. conc. HNO_3 and 1 ml. conc. HCl and dry on steam bath.
6. Place beaker in muffle furnace at 400°C . for 15 minutes.
7. Return to steam bath, add 20 ml. 2 percent acetic acid, and loosen ignited residue with rubber policeman.
8. After ten minutes, filter through clean, 7 cm. Whatman No. 40 filter paper into a 50-ml. volumetric flask. Repeat step 7 twice more with 10-ml. portions of 2 percent acetic acid and filter into same volumetric flask. Rinse beaker and paper with five 2-ml. portions of distilled water and, when flask and contents have cooled dilute to 50 ml. mark. Calcium and sodium are determined in this extract.

B. Exchange capacity.

1. To the extracted clay in the 50-ml. centrifuge tube add 30 ml. 95 percent ethanol, stir until completely dispersed, centrifuge as before and decant through same filter (III.A.3.). Repeat ethanol washing until filtrate tests free of ammonium ions (use Nessler's reagent). Decant and allow complete drainage each time. Discard filtrate.
2. Transfer entire sample to Kjeldahl flask, washing tube with distilled water and aid of rubber policeman. Rinse tube with fine stream of water.
3. Transfer filter paper with any adhering clay to same Kjeldahl flask. Add 250 ml. distilled water, 1 to 2 grams MgO , and connect to distillation apparatus. Collect distillate in 250-ml. flask containing 25 ml. saturated boric acid and several drops of brom cresol green-methyl red indicator. Continue distillation until about 200 ml. have passed over.
4. Titrate with 0.05 N. H_2SO_4 and calculate exchange capacity:
$$\frac{ml.H_2SO_4 \times normality \times 100/wt.clay \text{ in aliquot}}{= m.e./100 \text{ grams clay}}$$

C. Exchangeable sodium determination.

1. Transfer 10 ml. (or sufficient for 0.02 to 0.2 m.e. Na) aliquot of the extract (III.A.8.) to a 150-ml. beaker. Slowly evaporate to dryness on the hot plate. Cool, take up with 2 ml. warm distilled water and add slowly with constant stirring 30 ml. of zinc uranyl acetate reagent (Regional Salinity Laboratory specifications) in 10 ml. portions. Stir for one minute, and let stand for 24 hours.
2. Filter through an M-type sintered glass filter (long neck) with suction and wash the adhering precipitate from the beaker with five 2-ml. portions of the precipitating reagent, allowing it to be completely removed each time by suction. Finally, wash the precipitate using spray-type pipette assembly described by Kelley and coworkers (26) with five 2-ml. portions of 95 percent ethanol saturated with sodium zinc uranium acetate. Do not use absolute alcohol. Discard washing and replace with a clean flask.
3. Dissolve the precipitate in 100 ml. of hot, boiled distilled water, add five drops of phenolphthalein and 10 ml. 0.1 N NaOH (use pipette). Heat the solution to incipient

boiling and titrate with 0.1 N HCl. Continue incipient boiling and titration until end point persists. Calculate milliequivalents of sodium per 100 grams of clay:

$$\left\{ \left[\text{ml. NaOH} \times \text{norm.} \right] - \left[\text{ml. HCl} \times \text{norm.} \right] - \right. \\ \left. \text{m.e. NaOH required for blank} \right\} / 10 \times 50/10 \\ \times 100/\text{wt. of clay in original 10 ml. sus-} \\ \text{pension} = \text{m.e. Na/100 grams of clay.}$$

D. Exchangeable calcium determination.

1. Transfer 25-ml. aliquot of the extract (III. A.8.) to a 100-ml. beaker, add a few drops of methyl orange. Add 1 ml. of 1 N. oxalic acid and heat to boiling. Neutralize with approximately 7 N. NH_4OH (1:1).
2. Add an excess of 1 N. oxalic acid with constant stirring (about 10 ml.).
3. Add 7 N. NH_4OH to the hot solution until just alkaline to methyl orange. Cool and let stand several hours (further additions of 7 N. NH_4OH may be necessary during cooling to keep the solution faintly alkaline).
4. Filter through Whatman No. 40 paper and wash thoroughly with water until free of chlorides.
5. Puncture tip of filter paper and wash the precipitate into a clean 250-ml. beaker. Add 5 ml. conc. H_2SO_4 to approximately 40 ml.

distilled water in a 50-ml. flask, mix and bring volume to 50 ml. Pour this hot solution through the filter paper. Wash with water or until volume is approximately 100 ml. in beaker.

6. Heat nearly to boiling and titrate with 0.05 N. KMnO_4 solution over a white base stand to a faint pink color. When end point is reached drop the filter paper into the solution and stir thoroughly. Complete the titration quickly to the first definite pink end point. Calculate milliequivalents of calcium per 100 grams of clay:

$$\begin{aligned} & (\text{ml. KMnO}_4 - \text{ml. blank}) \times \text{norm.} \times 50/25 \times \\ & 100/\text{wt. of clay in original 10 ml. suspension} \\ & = \text{m.e. Ca/100 grams of clay.} \end{aligned}$$

IV. Equilibrations and pH determinations

A. Clay- CO_2 - H_2O systems.

1. Transfer 30 ml. of 2 percent clay suspension to a 100-ml. wide-mouthed jar. Stopper with a 3-holed, rubber stopper fitted with a glass or disc-type bubbler, and capable of supporting the large electrodes of the Beckman pH meter in the other two holes. Fasten the jar in a constant temperature water bath at 20°C .

2. Prepare 0.001 N. NaOH by diluting 2 ml. of 0.5 N. NaOH to one liter. Check normality. Transfer 25 ml. of solution to a 100-ml. wide-mouthed jar and add several drops of phenolphthalein. Affix 3-holed stopper with bubbler and pass through sufficient pure CO₂ to reduce the pH to about 6.0 (color change).
3. Connect line from supply tank through valves, water bottle and test solution to train of samples. Commence equilibration with approximately 0.06 percent CO₂-air mixture (pass pure CO₂ into pressure tank for a few seconds). Record pH readings about every six hours during the day and twelve overnight (0700, 1300, 2000, 0700) for a period of 48 hours. Continue to 60 hours if successive readings do not check within 0.05 pH unit.
4. After final readings have been taken, turn on pressure tank motor, add pure CO₂ to the tank for 40 seconds, and build up tank pressure with air to 120 lbs./sq.in. Commence equilibration with second CO₂-air mixture(48 hrs.).
5. Repeat equilibration procedure at third CO₂ pressure level by adding pure CO₂ to the pressure tank for two and one-half minutes, then filling with air to 120 pounds. Replace

0.001 N NaHCO_3 test solution with 0.0107 N solution. pH readings should be taken every three to four hours for a period of 24 hours.

5. The suspensions are finally equilibrated with pure CO_2 for a period of 6 hours, and pH readings are taken at second, fourth and sixth hours.
6. Barometric pressure and temperature in the laboratory are recorded during the final hours of each equilibration.
7. Plot results graphically, pH (ordinate) against log partial pressure of CO_2 to obtain pH curves (CO_2 pressure obtained by use of test solution data applied to standard curve given by Wilson and coworkers (65)).

B. Clay- CaCO_3 - CO_2 - H_2O systems.

1. Weigh out 50 milligrams of Baker's C.P. Special CaCO_3 and add to the wide-mouthed jar containing the clay suspension previously equilibrated. Perform equilibration and pH determinations as previously outlined (IV.A.)

C. Complex systems.

1. Add one milliliter of 1 N. NaCl and repeat equilibration at four CO_2 pressure levels.
2. Finally, add 300 milligrams of Baker's C.P. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and repeat equilibrations.

APPENDIX B

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Table A.--SAMPLE DATA SHEET: EQUILIBRATION OF SYSTEM
FORT COLLINS CLAY-CaCO₃-CO₂-H₂O AT 20°C

TIME (HRS.)	PERCENT SODIUM						NaHCO ₃ Test Soln.
	90	39	13	10	8	0.4	
I. Start 0900, 5Mar49	pH						(0.001N)
5	8.47	8.31	7.99	8.00	7.98	7.92	7.95
8	8.55	8.38	8.00	7.98	8.00	7.88	7.95
24	8.59	8.42	8.10	8.17	8.10	7.98	8.01
29	8.66	8.45	8.10	8.20	8.10	7.99	8.00
34	8.65	8.47	8.12	8.21	8.12	7.99	8.02
48	8.66	8.43	8.11	8.19	8.11	7.97	8.00
Eq.pH	8.66	8.44	8.11	8.20	8.11	7.98	8.01
Log ∂ CO ₂							¹ -0.34
II. Start 0900, 7Mar49	pH						
4	8.17	7.52	7.37	7.22	7.18	7.16	7.01
8	7.96	7.44	7.29	7.26	7.21	7.18	6.90
24	7.68	7.45	7.31	7.32	7.22	7.16	6.88
30	7.69	7.44	7.30	7.32	7.22	7.18	6.90
Eq.pH	7.69	7.44	7.30	7.32	7.22	7.17	6.90
Log ∂ CO ₂							0.77
III. Start 2200, 8Mar49	pH						(0.0107N)
12	8.25	6.88	² 7.19	6.77	6.71	6.71	6.97
17	6.95	6.81	6.65	6.68	6.67	6.68	7.00
22	6.91	6.82	6.68	6.69	6.69	6.69	6.98
36	6.91	6.81	6.68	6.71	6.70	6.70	6.98
Eq.pH	6.91	6.81	6.68	6.70	6.69	6.68	6.98
Log ∂ CO ₂							1.69
IV. Start 1230, 10Mar49	pH						³ B.P.
1	5.87	5.85	5.79	5.76	5.75	5.78	637.8
3	5.88	5.88	5.79	5.81	5.81	5.81	637.5
5	5.88	5.88	5.81	5.80	5.85	5.81	637.0
Eq.pH	5.88	5.88	5.80	5.79	5.83	5.81	637.4
Log ∂ CO ₂							2.80

Table from page 86, data book.

¹Calculated from Wilson(65)equation: pH = 7.67-log ∂ CO₂

²Bubblers failed and clogged overnight.

³Barometric pressure at room temperature expressed in millimeters of mercury.

Table B.--EQUILIBRATION DATA OF BENTONITE CLAY SYSTEMS AT 20°C. [Summary of data collected 1/28/49-2/28/49]

Log pCO ₂	PERCENT SODIUM					
	96	59	19	9	8	5
pH of system: clay-CO ₂ -H ₂ O						
-0.61	8.35	8.20	7.92	8.22	8.15	8.10
-0.53	8.32	8.05	8.18	8.13	8.11	8.28
0.07	7.80	7.64	7.65	7.66	7.58	7.80
0.78	7.18	7.06	7.01	7.13	7.05	7.36
1.67	6.29	6.10	6.24	6.24	6.20	6.60
2.80	5.21	5.05	5.12	5.17	5.16	5.41
pH of system: clay-CaCO ₃ -CO ₂ -H ₂ O						
-0.33	8.58	8.34	8.18	8.15	8.01	8.13
0.81	7.72	7.45	7.40	7.32	7.14	7.32
1.75	6.95	6.76	6.70	6.68	6.48	6.67
2.80	5.95	5.81	5.77	5.75	5.57	5.75
pH of system: clay-CaCO ₃ -NaCl-CO ₂ -H ₂ O						
-0.34	8.52	8.28	8.22	8.01	8.20	7.95
0.85	7.65	7.37	7.31	7.28	7.16	7.24
1.67	6.99	6.83	6.76	6.80	6.62	6.78
2.80	5.90	5.82	5.78	5.80	5.60	5.79
pH of system: clay-CaCO ₃ -NaCl-CaSO ₄ -CO ₂ -H ₂ O						
-0.38	7.90	7.96	7.91	7.69	7.89	7.85
0.78	7.19	7.22	7.15	7.11	7.12	7.13
1.62	6.75	6.72	6.76	6.70	6.62	6.76
2.80	5.73	5.69	5.71	5.76	5.59	5.72

Table C.--EQUILIBRATION DATA OF FORT COLLINS CLAY SYSTEMS
AT 20°C. [Summary of data collected 2/28/49-3/19/49]

Log ∂CO_2	PERCENT SODIUM					
	90	39	13	10	8	0.4
pH of system: clay-CO ₂ -H ₂ O						
-0.34	8.22	8.20	8.02	7.92	7.82	7.85
0.85	7.28	7.12	6.98	6.96	6.88	6.88
1.66	6.64	6.49	6.32	6.31	6.24	6.26
2.80	5.55	5.41	5.28	5.26	5.22	5.24
pH of system: clay-CaCO ₃ -CO ₂ -H ₂ O						
-0.34	8.66	8.44	8.11	8.20	8.11	7.98
0.77	7.69	7.44	7.30	7.32	7.22	7.17
1.69	6.91	6.81	6.68	6.70	6.69	6.68
2.80	5.88	5.88	5.80	5.79	5.83	5.81
pH of system: clay-CaCO ₃ -NaCl-CO ₂ -H ₂ O						
-0.35	8.75	8.61	8.52	8.38	8.44	8.36
0.45	8.13	8.04	8.02	8.01	7.96	7.95
1.50	7.06	6.94	6.92	6.82	6.90	6.84
2.80	5.89	5.89	5.88	5.83	5.83	5.83
pH of system: clay-CaCO ₃ -NaCl-CaSO ₄ -CO ₂ -H ₂ O						
-0.51	8.22	8.18	8.21	8.01	8.15	8.12
0.82	7.21	7.20	7.23	7.18	7.17	7.17
1.45	6.82	6.82	6.83	6.82	6.81	6.83
2.80	5.83	5.83	5.81	5.80	5.81	5.81

Table D.--EQUILIBRATION DATA OF GRAND JUNCTION AREA SOIL
57A CLAY SYSTEMS AT 20°C. [Summary of data collected
3/19/49-4/10/49]

Log ∂CO_2	PERCENT SODIUM					
	90	50	39	22	6	3
pH of system: clay- CO_2 - H_2O						
-0.34	7.77	7.74	7.45	7.78	7.21	7.68
0.71	6.85	6.90	6.65	6.74	6.60	6.75
1.67	6.20	6.32	6.07	6.12	6.14	6.20
2.80	5.21	5.28	5.05	5.12	5.10	4.99
pH of system: clay- CaCO_3 - CO_2 - H_2O						
-0.45	8.74	8.47	8.30	8.35	8.12	8.27
0.48	7.88	7.89	7.65	7.59	7.49	7.53
1.45	7.16	6.99	7.02	7.00	6.81	6.87
2.80	6.01	5.91	5.97	5.99	5.81	5.84
pH of system: clay- CaCO_3 - NaCl - CO_2 - H_2O						
-0.35	8.65	8.47	8.40	8.30	8.20	8.32
0.70	7.76	7.47	7.43	7.37	7.30	7.32
1.55	7.17	6.90	6.88	6.88	6.79	6.78
2.80	6.02	5.89	5.93	5.98	5.89	5.85
pH of system: clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O						
-0.32	8.13	8.06	8.03	8.06	7.97	7.98
0.79	7.30	7.21	7.20	7.23	7.20	7.20
1.62	6.82	6.77	6.75	6.77	6.71	6.72
2.80	5.92	5.84	5.90	5.92	5.86	5.79

Table E.--EQUILIBRATION DATA OF KAOLIN CLAY SYSTEMS AT 20°C. [Summary of data collected 4/15/49-5/5/49]

Log ∂CO_2	PERCENT SODIUM					
	100	37	12	9	3	2
pH of system: clay- CO_2 - H_2O						
-0.33	7.72	7.42	7.51	7.55	7.29	7.41
0.78	6.72	6.62	6.78	6.78	6.42	6.68
1.65	6.00	5.92	6.18	6.05	5.68	5.95
2.80	5.00	4.88	5.06	4.96	4.68	4.92
pH of system: clay- CaCO_3 - CO_2 - H_2O						
-0.28	7.88	7.98	7.98	8.01	7.92	7.93
0.87	7.14	7.18	7.17	7.20	7.16	7.15
1.56	6.78	6.76	6.77	6.78	6.78	6.75
2.80	5.88	5.78	5.82	5.88	5.90	5.80
pH of system: clay- CaCO_3 - NaCl - CO_2 - H_2O						
-0.39	7.98	8.12	8.11	8.18	8.09	8.10
0.39	7.48	7.56	7.57	7.53	7.57	7.52
1.49	6.78	6.80	6.81	6.81	6.85	6.80
2.80	5.83	5.89	5.90	5.81	5.99	5.90
pH of system: clay- CaCO_3 - NaCl - CaSO_4 - CO_2 - H_2O						
-0.32	7.89	8.00	7.93	8.00	7.95	7.96
0.66	7.21	7.20	7.16	7.18	7.27	7.18
1.62	6.60	6.64	6.52	6.48	6.68	6.57
2.80	5.80	5.71	5.71	5.68	5.80	5.69

Table F.--EQUILIBRATION DATA OF GRAND JUNCTION AREA SOILS
AT 20°C. [Summary of data collected 4/11/49-5/24/49]

Log	SOIL NUMBER					
∂CO_2	5A	6A	8A	13A	16A	26A
pH before leaching: 1 to 5 dilution						
-0.32	8.29	8.32	8.38	8.75	8.62	8.23
0.77	7.47	7.69	7.80	7.75	7.61	7.72
1.69	6.85	7.07	6.99	7.03	6.88	6.93
2.80	6.13	6.18	6.28	6.25	6.10	6.22
pH after leaching: 1 to 5 dilution						
-0.35	8.26	8.38	8.38	8.66	8.33	8.35
0.69	7.65	7.72	7.67	7.79	7.61	7.62
1.71	6.83	6.89	6.87	6.97	6.80	6.89
2.80	6.12	6.13	6.13	6.19	6.08	6.12
pH before leaching: 1 to 50 dilution						
-0.32	8.29	8.32	8.38	8.40	8.25	8.30
0.57	7.49	7.51	7.56	7.57	7.44	7.50
1.65	6.80	6.81	6.88	6.79	6.68	6.84
2.80	5.92	5.96	6.04	5.75	5.63	6.00
Log	SOIL NUMBER					
∂CO_2	15C	23B	29A	34B	45C	57A
pH before leaching: 1 to 5 dilution						
-0.29	8.50	8.59	8.16	8.03	8.12	7.83
0.79	7.72	7.75	7.51	7.40	7.50	7.29
1.51	7.15	7.17	6.99	6.97	7.01	6.82
2.80	6.27	6.27	6.18	6.15	6.20	6.08
pH after leaching: 1 to 5 dilution						
-0.30	8.48	8.58	8.30	8.32	8.65	8.26
0.78	7.65	7.86	7.52	7.56	7.76	7.54
1.67	7.00	7.08	6.90	6.91	7.09	6.92
2.80	6.23	6.26	6.15	6.13	6.28	6.18

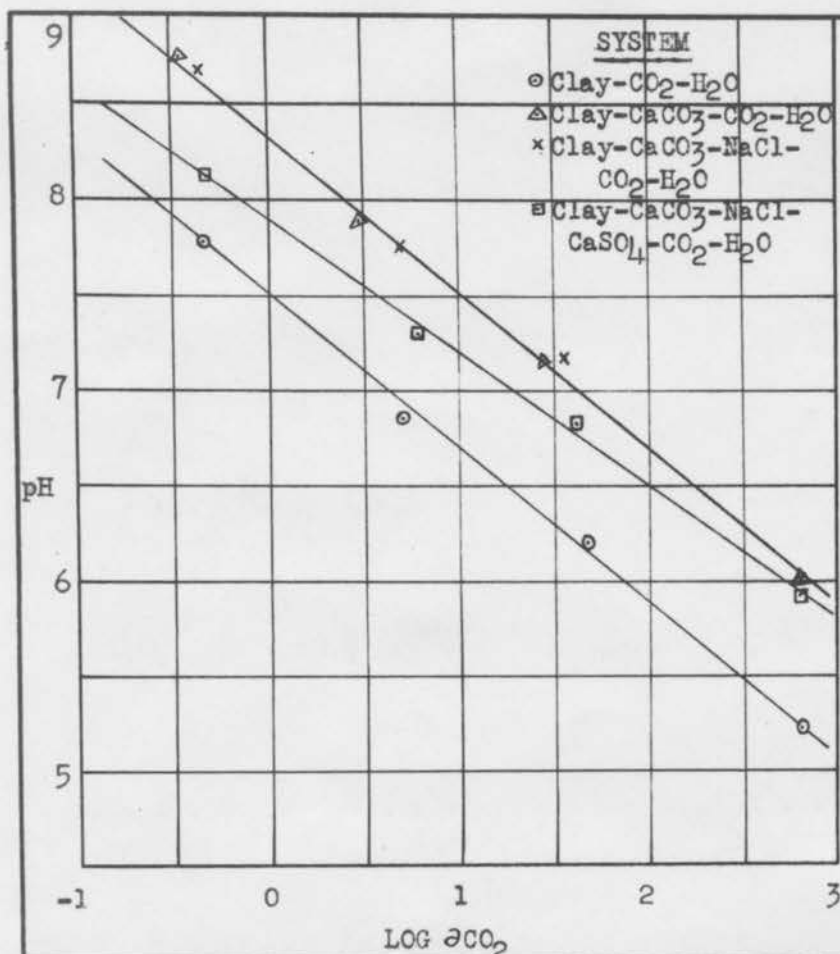


Fig. A.--The pH of a 90% Na-Grand Junction Area soil clay (57A) in various systems at CO₂ equilibrium.
[The clay to water ratio was 1 to 50]

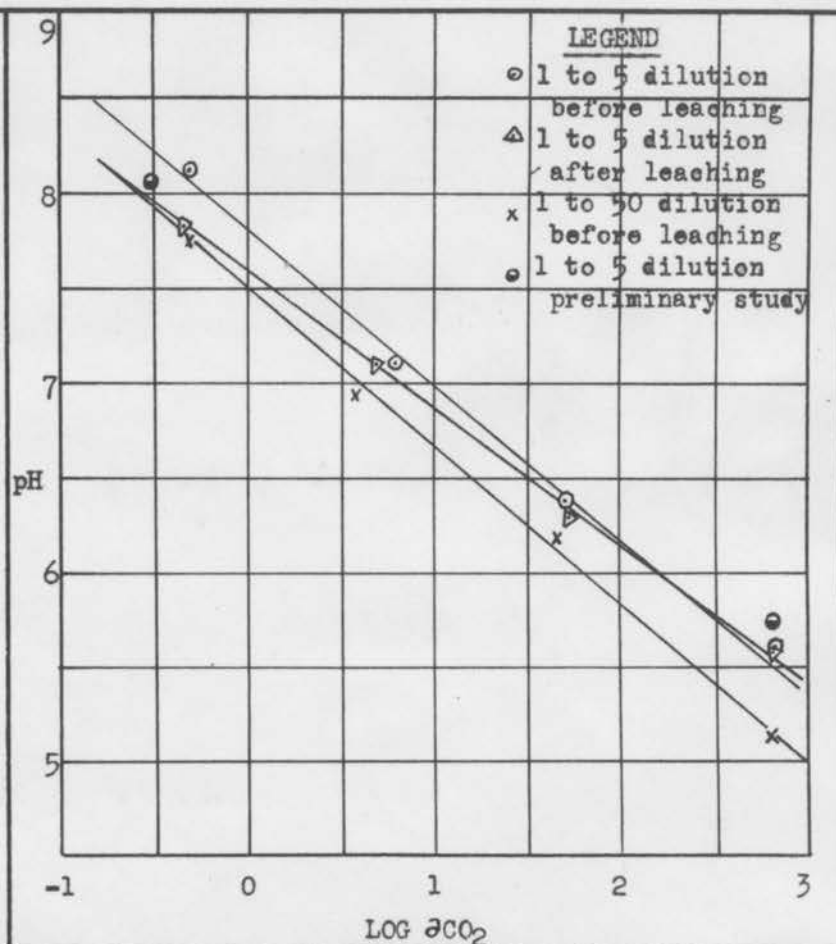


Fig. B.--The pH of Grand Junction Area soil 16A at CO₂ equilibrium.

[The soil to water ratio is indicated]

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