

AN ABSTRACT OF THE THESIS OF

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Title THE RELATIONSHIP BETWEEN CATION EXCHANGE CAPACITY, TOTAL
BASES, AND EXCHANGE ACIDITY IN CERTAIN OREGON SOILS

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Two soils representative of the coast and three representing the Willamette Valley have been studied for their general chemical characteristics. Exchange capacity and exchangeable cations were determined by the ammonium acetate and the BaCl_2 -triethanolamine buffer methods. Exchange capacity was also obtained from conductimetric titrations which were run on each soil before and after destroying the organic matter. Potentiometric titrations were run before and after leaching each soil with HCl. Lime requirement was determined by Woodruff's method and also obtained from the pH-lime curves.

The two coastal soils, Astoria and Clatsop, have lower pH and base saturation and higher organic matter content and exchange capacity than the Melbourne, Olympic, and Willamette soils from the valley. The Melbourne soil had the highest base saturation percentage and Astoria had the lowest. The amount of exchangeable aluminum was also higher in the coastal soils.

The amount of exchange capacity contributed to the organic fraction was 65 per cent in the Olympic and Willamette soils and 50 per cent in the other three. The value for exchange capacity by the different methods was in good agreement in the three valley soils before and after the organic matter was destroyed. In the coastal soils there was no agreement between methods in any case. This would indicate that in the latter two soils, type of clay mineral present may be more of an influence than in the former soils.

The potentiometric titration curves showed that the two coastal soils were well buffered and the valley soils were only slightly buffered. After the soils were leached with HCl the Melbourne soil was the only one which indicated a strong acid property.

The exchange properties of the soils as affected by additions of lime were studied by incubating the soils for four weeks with added increments of lime. With each added increment of lime the pH increased and exchangeable acidity decreased in each soil. The amount of lime to bring the soils to any given degree of base saturation

appeared to be proportional to the magnitude of the exchange capacity and inversely proportional to the degree of base saturation. At any given pH value there was a considerable difference in the degree of base saturation for these soils. This might well be a reflection of the type of minerals present in the different soils.

More lime was required to bring the two coastal soils up to pH 6.5 as indicated by the pH-lime relationship curve than that estimated by the Woodruff method. Consistent results were observed in the three valley soils. This suggests that the buffer solution at pH 7 as recommended by Woodruff was not strong enough to neutralize the acidity in the coastal soils.

There was good agreement between the two methods in the determination of the exchangeable bases. The BaCl_2 -buffer method gave much higher values of exchangeable acidity than did the ammonium acetate method. These values, when converted to tons of calcium carbonate, agree fairly closely with the amount of lime required to bring the soils to pH 7 when added directly to the soil. When lime was added above the saturation point the amount of exchangeable calcium as determined by the ammonium acetate method increased but remained relatively constant for the BaCl_2 -buffer method.

The various analysis seem to indicate that the Astoria and Clatsop soils contain predominantly 2:1 type clay minerals while the Olympic and Willamette soils contain predominantly the 1:1 type. The Melbourne soil exhibits properties more closely associated with the coastal soils.

THE RELATIONSHIP BETWEEN CATION EXCHANGE CAPACITY, TOTAL
BASES, AND EXCHANGE ACIDITY IN CERTAIN OREGON SOILS

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THE RELATIONSHIP BETWEEN CATION EXCHANGE CAPACITY, TOTAL
BASES, AND EXCHANGE ACIDITY IN CERTAIN OREGON SOILS

INTRODUCTION

All of the soils of Western Oregon are acid, varying only in degree. The summary of soil test results for 1953-55 from the Oregon State College Soil Testing Laboratory show, for example, that 74 per cent of the soils from the coastal counties had a pH of 5.4 or below (38, pp. 1-5). There were 98.5 per cent of the soils with a pH of 6.0 or below. In the Willamette Valley the same summary shows 38 per cent of the soils below pH 5.5 and 91 per cent below pH 6.1. Sixty-five per cent of the coastal soils require over four tons of lime per acre and 80 per cent of the valley soils need over two tons of lime per acre as determined by the Woodruff Method (63, pp. 53-63).

Lime is necessary for western Oregon agriculture. It has been estimated that there are over 900,000 acres of land in the coastal and Willamette Valley areas that are badly in need of lime (40, pp. 1-30). For the Willamette Valley alone it has been estimated that 1 1/2 million tons of lime are needed to reach optimum calcium levels in the soil and an additional 180,000 tons per year would be needed to maintain the level (39, pp. 1-75).

There are indications that the present lime requirement test as used by the Soil Testing Laboratory is not predicting as much lime as is actually needed for some soils to raise the pH to 6.5. The lime requirement test may show a need for 6-8 tons of lime when 10 to 12 tons may actually be required to raise the soil pH to 6.5.

This is particularly true for the coastal area but also to some extent for the Willamette Valley soils developed on residual material. It has also been noted that the sum of exchangeable bases and exchangeable hydrogen, as indicated by the Woodruff lime requirement test, fails to add up to the cation exchange capacity of certain soils. This indicates that either the methods used for exchangeable bases and/or lime requirement are unreliable or there is some factor in these soils that is not being taken into account.

It is the purpose of this thesis to study the various factors which may be involved in the chemical characteristics of certain acid soils and which relate to the above problems. The soils used in this study are the Astoria and Clatsop soils from the coast, the Melbourne and Olympic soils from the Willamette Valley "red hills" and the Willamette soil developed on alluvium in the Willamette Valley. These soils cover an appropriate range of the acid conditions found in western Oregon. The objectives are:

1. To determine the relationship between the cation exchange capacity, total bases, buffer properties and exchange acidity in these soils.
2. To correlate our present lime requirement test with the values obtained from the above analysis.

As there are indications from other workers in this field that the present ammonium acetate method for determining exchangeable bases and cation exchange capacity is not entirely satisfactory for all types of soils, this study includes a comparison with the BaCl_2 -triethanolamine buffer method.

Besides the chemical study on the original soils, all of the soils were incubated with different increments of added lime. This was done in order to obtain a more complete study of the pH-lime-base saturation relationship.

LITERATURE REVIEW

The Nature of Soil Acidity

Soil acidity is common in all regions where precipitation is high enough to leach appreciable amounts of exchangeable bases from the surface layers of soils. Soil acidity may also result from the removal of bases by plants, the decomposition of organic matter through micro-organism activity and fertilizer management.

Early concept. Cation exchange phenomena in soils have been known since the experiment of Thompson and Way in 1850 and soil acidity has been considered as an adsorption phenomenon by Wiegner and Gedroiz (18, pp. 1-18) since then. The pioneer work of Bradfield (3, pp. 2669-2678) clarified this concept. He separated acid clays by centrifugal methods and then titrated the fractions potentiometrically and conductometrically. After comparing the clays with gels of silicic acid, aluminum hydroxide and iron hydroxide he concluded that the colloidal material of an acid soil was itself an acid which ionizes to produce definite acidity titratable with strong bases. Soil acidity was presumed to be due to the acid alumino-silicate clay which behaved like a weak acid during the titration process. A number of studies performed more recently by Joffe and McLean (16, pp. 181-195) and Kelley and Brown (19, pp. 289-309) have been presented to support this concept.

Characterization of buffering properties based on titration

curves. Numerous studies have been carried out in attempts to characterize the nature of the buffer action and to estimate the buffering capacity of both the clay fraction isolated from the soil, and also the soil as a whole. This has been accomplished through the use of potentiometric or conductometric titration techniques. Baver (2, pp. 587-603), titrating soils with NaOH, has shown that the nature of soil buffer action is primarily dependent upon the inorganic colloidal clay acids. Organic colloidal acids were responsible for buffer action above the neutral point. Anderson and Byers (1, pp. 1-38) isolated the colloidal fractions from a number of soils representative of the great soil groups by acid dialysis and then titrated them with NaOH. They claimed that titration curves would prove to be a valuable aid in characterizing soil colloids. However, it was difficult to obtain reproducible results because the equilibrium between soil colloids and alkali added was not established quickly. Titration curves of the soil colloids closely resembled those of weak diacidic acid. The point of inflection occurred approximately 4 pH units above the initial pH of the acidoid and corresponded to the neutralization of the first hydrogen. Puri and Uppal (51, pp. 245-253) studied cation exchange in soils by alternately leaching the soils with a neutral salt and 0.05 normal hydrochloric acid. From the titration curves obtained when the H-saturated soil was titrated serially with sodium hydroxide, the acidoid equivalent or base exchange capacity was interpolated to a point 4 pH units higher

than the initial pH. Therefore, the neutralization point of soil colloids was not the same for all soils. They also found that when a neutral salt solution was shaken with an acid soil, a portion of the cation of the salt was taken up and an equivalent amount of free acid, which was called exchange acidity, was produced. The amount would be governed by the relative strength of the acid radical of the salt as compared to the soil acidoid. In effect a larger proportion of the base would be taken up by the soil from acetates than from chlorides.

Studies of exchangeable hydrogen based on clay mineralogy.

Marshall and Krinbill (24, pp. 1077-1090) have presented an interesting theory based on the cationic activities associated with the various clay minerals. When considering all exchangeable cations in soils, hydrogen is the most strongly adsorbed and consequently is the most difficult to replace by other cations. In clays having the 1:1 type lattice, exchangeable hydrogen is bonded more strongly to the oxygen atoms of the OH groups than those having 2:1 type. Hence, hydrogen saturated clays of the 2:1 type lattice are more extensively dissociated and show much lower pH values than those of the 1:1 lattice groups. The nature of the cation such as charge, ionic radii, degree of hydration, the associated anion, and the concentration of the salt solution used also influences the amount of hydrogen that can be extracted. Thus, for a given degree of neutralization of the clay acid with

different bases, the higher the degree of dissociation of the cation adsorbed on the clay the higher will be the pH of the clay suspension.

Exchangeable aluminum. Marshall and Krimbill (24, pp. 1077-1090) also recognized that after electro dialysis the reaction of the clay changed spontaneously in the direction of the neutral point. This clay acid, on treatment with neutral salts, generally exchanged aluminum as well as hydrogen, suggesting that electro dialyzed clays are really H-Al clays and are to a variable extent chemically unstable.

Mukherjee and Banerjee (36, p. 247), with alternating treatments on the soil with dilute acid and neutral salt solution have found that the sum of the displaced aluminum and iron ions decreases with progressive acid treatment, tending to a constant value. Slabaugh (57, p. 4462) reported titration data and heats of neutralization for acid bentonites prepared by electro dialysis and by columning through exchange resin. He found that the columned clay, in contrast to the electro dialyzed, gave results indicative of strong acid properties. The investigations of Harward and Coleman (15, pp. 181-188) have indicated that hydrogen-clay could be prepared by passage through a column of H-exchange resin or by leaching with normal hydrochloric acid, whereas, clays which were electro dialyzed or treated with dilute acids, were H-Al-clays with aluminum predominating. The acidic properties of the hydrogen and aluminum clays, as indicated by potentiometric

and conductometric titrations and by heats of neutralization were found to be quite different. Low (22, pp. 135-139) confirmed further that the initial inflection or break in the potentiometric and conductometric titration curves for bentonite prepared by saturating with different ratio of hydrogen and aluminum and by electro dialysis is due to the exchangeable Al displaced from the crystal lattice by hydrogen. In addition he postulated that the electro dialyzed bentonite was largely Al-clay instead of H-clay. According to these recent investigations, it would be expected that the buffering properties of acid soils appear to be dependent upon the quantity of aluminum.

Soil acidity contributed by the organic matter. In Kelley's review of literature, Hissink (19, pp. 289-309) suggested that humus which was mainly organic acids also played an important role in soil acidity in addition to the alumino-silicic acid. Many studies have been carried out on the buffering properties of the organic-colloidal materials isolated from soils by means of titration curves (1, pp. 1-38; 25, pp. 153-165; 50, pp. 165-175; 62, pp. 1-11). Results indicate certain general consistent characteristics in their titration curves; namely, the inflection points were not always pronounced and in a number of cases multiple inflections were evident. In general, these curves showed very slight change in slope. Moreover, organic colloids are amphoteric in nature and exert greatest buffering capacity in

the alkaline range.

It is interesting to note that Feustel's (12, pp. 1-41) studies using sodium hydroxide and barium hydroxide solution for determining the acidic properties of peat and muck have shown that the titration curves were similar in some cases but different in others. He explained this difference on the basis of different reactions between the acidic groups of the organic materials and the two bases. Based on the results obtained, Feustel stated that well characterized breaks might be observed analogous to the titration of ordinary weak acids if an extremely dilute suspension of electrolyzed peat or soil material were used. This break in slope of the curve was interpreted as the end point of the neutralization of the well defined acidity.

Relationship Between Cation Exchange Capacity, pH, Base Saturation and Their Determinations

Cation exchange capacity. Schofield (53, p. 29) has devised techniques for measuring the electric charges carried by clay particles, resulting from isomorphous substitution in the crystal lattice and the dissociation of H^+ from OH groups situated at the edges of the crystal. The former was called permanent charge by Schofield because it was presumed to be constant between pH 2.5 and pH 5; the dissociation of the latter from the OH^- groups start at pH 6 and become appreciable at pH 7. Therefore, he emphasized that unless one chooses to define the base exchange

capacity of the clay as the permanent negative charge carried by its particles, it can only have an arbitrary meaning under specified conditions.

From the standpoint of clay mineralogy it has been demonstrated by many investigators (5, pp. 32-137; 13, pp. 126-160; 23, pp. 101-119; 43, pp. 335-396) that discrepancies in results obtained by different methods for determining cation exchange capacity must be attributed not only to the pH but also to the characteristics of the clay minerals, nature of the bases used for extraction and their differences in tendency toward hydrolysis (54, pp. 13-24).

Schollenberger (54, pp. 13-24) suggested that ammonium acetate solution buffered at pH 7 for the determination of cation exchange capacity was favorable because this pH value is the conventional neutral point. It is near the pH of the bicarbonate-carbonate acid buffer system and is also a soil reaction most favorable to crop production in general. Moreover, ammonium acetate is equally hydrolyzed, weakly dissociated and ammonium adsorption is easy to determine. This might be the reason that ammonium acetate procedure has been widely used as a standard routine method for the measurement of cation exchange capacity.

It has been found by many investigators comparing the ammonium acetate method with other methods that there are certain disadvantages in using ammonium acetate for the exchange capacity measurement. Certain criticisms have been made by various investigators. These have been summarized below:

1. Low values of exchange capacity are obtained especially in the soil containing high organic matter and 1:1 type clay mineral. (31, pp. 289-304).
2. Ammonium acetate solution has been shown to dissolve free calcium carbonate if present in the system studied. (31, pp. 289-304).
3. Pratt, et al (49, pp. 365-368) presented data showing that there were differences between the cation exchange capacity as determined by the ammonium acetate procedure and the sum of the exchangeable cations. He reasoned that the disadvantage of the ammonium acetate reagent seemed to be that H^+ ions became part of the system that displaced the cations on the exchange complex.
4. Peech (45, pp. 25-37) stated that the low value of cation exchange capacity as determined by ammonium acetate resulted from the incomplete replacement of calcium and magnesium, the predominant cations in soils.
5. Shaw (55, pp. 437-451) indicated that the exchangeable hydrogen determined by the ammonium acetate methods was much lower than those obtained through the use of the other methods particularly on soils of moderate to high organic matter content.

Mehlich (30, pp. 429-445; 31, pp. 289-304) has developed a procedure for determining cation exchange capacity by using barium chloride-triethanolamine solution buffered at pH 8.2. The results

indicated that 0.2N barium chloride replaced adsorbed calcium efficiently from all soils and minerals studied. With increasing concentrations of calcium carbonate small but relatively constant amounts of calcium were brought into solution. The amount of exchangeable hydrogen replaced was appreciably higher than that obtained by the ammonium acetate procedure. Pratt and Halowaychuk (49, pp. 365-368), comparing several methods, concluded that if the concept of base saturation is used in the study of soils, the logical displacing solution for exchangeable hydrogen should be highly buffered at or above the pH of the soil when 100 per cent base saturated with calcium; this being the dominant cation on the exchange complex. The pH values of soil samples that meet these specifications are usually between 7.6 and 8.2. On this basis it appears that the barium chloride-buffer at pH 8.2 for displacement of exchangeable hydrogen is justified. It would also seem the logical solution for the determination of the exchange capacity. The data of Mehlich (30, pp. 429-445; 31, pp. 289-304) and Hanna and Reed (14, pp. 477) substantiate this conclusion. This method has been questioned by Shaw (56, pp. 421-443) through the fact that triethanolamine, an organic cation, might exert some specific effect upon soil complex though Mehlich (28, pp. 115-123) claimed that it would not.

It has been suggested by Low (22, pp. 138-139) recently that on account of the ability of barium chloride to replace a definite amount of exchangeable Al from clay mineral, that different values

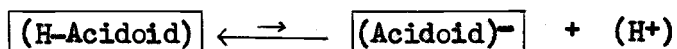
in cation exchange capacity (as determined by different methods) might be partly attributed to the differences in Al replacement at crystal edges and corners.

Another procedure for determining cation exchange capacity, was proposed by Mortland and Meller (35, pp. 363-364) and involves the use of conductimetric titrations of soil. This method is based on the relative mobility of the ions during titration. A soil saturated with barium is titrated conductimetrically with magnesium sulfate. Results indicated that this method was consistent with those obtained by the ammonium acetate and sodium acetate methods on prairie soils and soils containing 0.6 to 6.7 per cent of lime.

Measurement of pH. After a thorough survey of literature, Reed, et al (52, pp. 97-107) concluded that the pH value is unreliable when determinations are made on soils with moisture content corresponding to the moisture equivalent or below. Within the entire range of moisture content from the moisture equivalent to a soil-water ratio at 1:5, the effect of dilution was to increase the pH of the soil suspension regardless of the initial pH value of the soil. Upon further dilution of the 1:5 soil-water suspension the pH remains fairly constant.

Mattson and Wiklander (26, pp. 109-152) have proposed a theory based on the Donnan equilibrium principle to explain the effects of dilution and addition of neutral salts on the pH value of the soil suspension. Since the micellar solution contains the swarm ions

together with the ions of the free electrolytes, the concentration of the micellar solution is always greater than that of the outside solution. However, the concentrations of the two solutions become almost equal at high concentrations. It follows that on dilution of such a system the outside solution is diluted much more than the inside. The outside solution becomes relatively diluted to the extent that the equilibrium is deflected toward a greater entrance of divalent ion and H^+ .



From thermodynamic considerations as given by Overstreet (41, pp. 265-270), it can be shown that the chemical potential and hence the activity of the hydrogen ions must be greater in the micellar solution than in the intermicellar solution, so the pH of the clay suspension should increase as the proportion of intermicellar liquid in direct contact with the electrode increases.

Recently Peech (47, pp. 214-222) and Coleman, et al (9, pp. 106-114) found that soil pH as ordinarily measured in a stirred suspension or in a paste cannot be interpreted in terms of H^+ ion activity. The e.m.f recorded in such a measurement includes both the potential drop across the glass membrane which is controlled by the activity of H^+ and the potential drop across the salt bridge interface. In effect the junction potential due to the different mobilities of K^+ and Cl^- in the soil suspension can thus cause error in pH measurement. This junction potential can

be minimized by adding 1 N KCl solution to the system.

Relation between base saturation and pH. Pierre and Scarseth (48, pp. 99-114) stated that soils of the same reaction may vary considerably in their base saturation. In general, the highly weathered soils have a lower degree of base saturation at given pH values than less weathered soils. It was also found that the strength of the acids present was quite different from different soils. Highly weathered soils were generally found to have weaker acids than less weathered soils. A good correlation was obtained between the activity of soil acids and the percentage of base saturation at pH 4.8. Mehlich (29, p. 50) studied the relationship between base unsaturation and pH on several exchange materials. His results indicated that 2:1 type clay minerals represent strong acid properties and that 70 per cent neutralization occurred at about pH 5.4 and 100 per cent at pH 7.4. In 2:1 type clay colloids and organic base exchange materials, neutralization was practically complete at pH 7.0 - 7.5 whereas neutralization is only 50-80 per cent complete at these pH values for 1:1 type clays. Though the exchange capacity differed greatly with different exchange materials, the base saturation and pH relationship was not similarly affected. The presence of organic matter may modify this relationship. Peech (44, pp. 473-485) showed that in the pH range from 4.5 to 6.5 there was a linear relationship between the pH value of the soil and its degree of base saturation. The results

of Morgan (34, pp. 145-149) on Connecticut soils showed a general relationship between base saturation and pH. Mattson (26, p. 152) arrived at the conclusion that the pH, the concentration and the composition of the soil solution and the capacity of the soil to bind bases at a given pH are interdependent variables.

Lime Requirement

Titration method. Veith (10, p. 25) titrated soil with calcium hydroxide to the phenolphthaleim end point. This method, as would be expected, gave high results. Dunn's method (11, pp. 341-351) was based on a serial potentiometric titration of the soil with calcium hydroxide using a glass electrode for the pH measurement. He stated that this titration curve method gave reliable information on the amounts of lime required to bring acid soils to certain pH ranges.

Extraction of exchangeable hydrogen with some salt solution.

A method proposed by Jones (17, p. 29) involving the use of calcium acetate solution buffered at pH 4.76 would be expected to give low results on heavier acid soils for the pH was too low to effect complete replacement of exchangeable hydrogen. Brown (7, pp. 353-357) used neutral ammonium acetate as an extracting solution followed by the determination of the pH value of the extract by means of a glass electrode. Since the ammonium acetate solution was buffered at pH 7, the change in pH is small and must be measured very accurately.

Estimation of exchangeable hydrogen with buffer solution.

Based largely upon Bradfield's concept of calcium carbonate equilibrium at pH 8.4, Mehlich (32, pp. 162-166) advocated the use of a barium chloride triethanolamine solution highly buffered at pH 8.2 for the determination of exchangeable hydrogen. It was reported that this buffer solution replaces hydrogen efficiently. Woodruff's method (63, pp. 53-63) of testing soil for lime requirement is based on the estimation of the exchangeable hydrogen of the soil by combining the use of the glass electrode and concept of depression of pH of a buffered solution consisting of calcium acetate and p-nitrophenol. Each tenth of a pH unit depression corresponds to a calcium carbonate equivalent of 1000 pounds per acre. The range of depression in pH is limited from 7.0 to 6.0.

Use of carbon dioxide and calcium carbonate and bicarbonate.

Bradfield and Allison (4, pp. 8-15) defined a calcium saturated soil as one which was in equilibrium with an excess of calcium-carbonate at the partial pressure of carbon dioxide existing in the atmosphere. In a more recent paper Bradfield (4, pp. 8-15) studied the physico-chemical relations of soil calcium and found that the amount of calcium tied up by clay was independent of the amount of calcium hydroxide added once the saturation point was reached. After the saturation point was reached the amount of calcium present as calcium-bicarbonate also remained constant and

the amount of calcium adsorbed by clay also remained constant. Thus any further increase in the amount of calcium added was converted into a solid phase calcium carbonate.

Jensen (56, pp. 421-443) introduced a method for the titration of acidic soils with calcium hydroxide solution followed by equilibration with partial CO_2 pressure of the atmosphere. The buffering curve obtained by plotting pH versus added increments of calcium hydroxide was the basis for predicting the lime requirement.

Recently Patel and Truog (42, pp. 41-44) introduced the calcium-bicarbonate-soil reaction method as a basis for estimating the lime requirement of soils. The procedure is essentially a modification of the procedure proposed by MacIntire which consisted of evaporating a calcium-bicarbonate-soil suspension to a thin paste on a steam bath and determining the extent of reaction between soil and calcium carbonate by an analysis for the residual-calcium carbonate. The only modification in the new procedure is that the soil suspension is evaporated to dryness instead of a thin paste. It was claimed that the results obtained by the modified procedure does not vary more than one tenth ton per acre from the results obtained in the field.

Rates of reaction. Metzger (33, pp. 377-383) studied the rates of reaction between soils and lime added by incubating the soils with finely divided soil-liming materials under an optimum moisture content at 30°C . Results indicated that the hydrated lime

was probably completely carbonated before the first week.

Shaw (56, pp. 421-443) stated that the reasons responsible for abandonment of the calcium-carbonate or bicarbonate procedure might have been because:

- a. The soil-calcium carbonate reaction appeared to be continuous and was lacking in precision.
- b. The lime requirement indications proved to be excessive from the standpoint of practical agriculture.

In a recent investigation of the reaction speed between different soils and the incorporated calcium carbonate under different moisture and temperature conditions, Shaw presented data which indicated that under moistened conditions and room temperature, the reaction beyond the two-week period progressed at a very slow rate. Moreover, the occasional sudden upsurges in reaction rate might have been due to unrecognized disturbing effects. An appreciable part of the periodic calcium carbonate decomposition was postulated by Shaw to be due to the neutralization of the biologically engendered acids, chiefly HNO_3 .

DESCRIPTION OF SOILS

Coastal Soils

The area from which the Astoria and Clatsop soils were taken has a mild, temperate and equable climate. The mean annual temperature is about 51° F with a mean winter temperature of about 42° F. The mean annual rainfall is 77.46 inches. Most of the rainfall occurs during the fall and winter, the wet season beginning in October and extending through April. The distribution of rainfall along the coast is favorable for growing grass and forage (59, pp. 26-34).

The Astoria soil was taken from the hill on the John Jacob Astor Experiment Station and is mapped as Astoria loam. The surface soil is dark brown and well supplied with organic matter and contains iron concretions. The structure of this soil is beautifully granulated. This is a well drained soil developed from residuum from sedimentary rocks. It is very acid with the pH decreasing with depth, a nearly uniform texture with depth and friable consistence to greater than 60 inches depth. Because of greater rainfall and warmer winter temperature, the soils are more completely leached and as a result are not so fertile for general farm crops and need more fertilizer and lime for correction of high acidity.

The Clatsop soil, mapped as a silt loam, was taken from the tideland area near Astoria. This series occupies a considerable acreage of coastland that is affected by tides. Drainage is poor

because of the high water table and the heavy textured subsoil. The surface soil is yellowish brown, brownish gray, or gray mottled with orange or rusty brown. This soil is developed from recent alluvium at tide level. Bent grows on the area where drainage is developed and the soil was taken.

Valley Soils

The climate of this area is characteristic of that of the northwest Pacific Coast region. The winter is mild and rainy and the summers are comparatively dry, cool and pleasant. The rainy season includes the winter, a part of the fall and most of the spring. The mean annual precipitation is 44.03 inches. The mean annual temperature is 51.6° F ranging from 90° F. to -11° F (20, p. 1665).

The Melbourne soil was taken from east of Dallas, Polk County. It is a brown to light brown friable silty clay loam. The series name is not correct by present concepts. The organic matter is relatively low and pH is higher as compared to the coastal soils. This is well drained soil developed from residuum from sedimentary rocks. The surface soil is friable when moistened but hard when it is dry and maximum clay content occurs in the subsoil. Wheat and oats are the principal crops on this soil (8, p. 1448).

Olympic soil was taken from the Red Soils Experimental Area near Oregon City. The series name is not correct by the present concepts. The surface soil consists of a dull-reddish brown silt loam. It is a friable well-drained soil with a nearly uniform

texture with depth. The parent material from which this soil was developed is unknown. The organic matter is relatively low and pH is higher than those of the coastal soils (20, p. 1665).

The Willamette soil was taken from the George R. Hyslop Experimental Farm in Benton County. The name of this soil is not correct by present concepts. It is a moderately well-drained catenary associate of Willamette, developed from water deposited silty material. The surface soil is moderately dark colored and is friable when moist but hard when dry. The clay content increases with depth and in the lower subsoil is mottled. Cereals are the dominant crops on this soil. The organic matter is relatively low and pH is higher than those of the coastal soils (8, p. 1448).

METHODS OF ANALYSES

Soil Reaction

The pH values of the soils were measured in a 1:1 soil-water paste using a Beckman Model N pH meter with a glass electrode.

Organic Matter

The percentage of organic matter was determined by the chromic acid method as modified by Walkley and Black (61, pp. 29-37).

Determination of Aluminum

The aluminum extracted by the sodium acetate solution recommended by Peech (46a, p 167) was determined colorimetrically in presence of aluminon (ammonium salt of aurintricarboxylic acid).

Cation Exchange Capacity

The exchange capacity was determined by the ammonium acetate method proposed by Schollenberger (54, pp. 13-24), the $BaCl_2$ -buffer method recommended by Mehlich (30, pp. 429-445) and the conductometric titration method described by Mortland and Mellor (35, pp. 363-364). An Industrial Instrument Model RD-15 solu-bridge with a dipping type cell was used for the latter. All analyses were done in triplicate.

These determinations were made on both the original soils and after treatment with 10 per cent hydrogen peroxide (60, p. 109) to remove the organic matter. After treatment with peroxide the clay fraction in the soils seemed to have become completely dispersed

and hence became very sticky, consequently it was extremely difficult to handle during the leaching process on the Buchner funnel by means of ordinary suction. In such cases the peroxide-treated soil had to be washed by successive centrifugation after additions of leaching solution. It is advisable, however, to leach the H_2O_2 -treated soils with the leaching solution on the Buchner funnel without using suction if time is available.

Determination of Exchangeable Cations

The exchangeable cations were determined in triplicate in the ammonium acetate and $BaCl_2$ -buffer leachates as described above. In the former method the total bases were analyzed with a Beckman Model B flame photometer and the exchangeable acidity was obtained by difference. In the latter the procedure of Mehlich (30, pp. 429-445) was followed with the exception that 4.2 per cent (1.5N) H_2SO_4 was used instead of 1 per cent H_2SO_4 as recommended by Mehlich. It was somewhat difficult to obtain a definite end point in the presence of 1 per cent H_2SO_4 and in some instances a slightly brown or yellowish color appeared. The septavalent manganese apparently was reduced to the quadrivalent state and this caused the precipitation of hydrated manganese dioxide during the titration under a feebly acid condition (21, pp. 581-582). It should be noted also that calcium coprecipitates as calcium sulfate when H_2SO_4 is added to remove the barium present in the leaching solution. In order to minimize this error a correction factor was made by analyzing the solutions with

known amounts of calcium in the presence of barium. The efficiency of recovery of calcium was 87 per cent as compared to 90-95 per cent which Mehlich obtained.

Titration Curves of the Soils

The potentiometric titration curves were made on these soils by titrating a 1:10 soil-water mixture directly with 0.1N NaOH and plotting the pH values after each addition. The readings were made after stirring for 5 minutes with a magnetic stirrer, this time taken as an arbitrary criteria for the system to attain equilibrium.

Titration curves were made on both the original soils and soils treated with N HCl. Each soil was leached with 100 ml N HCl in order to remove the exchangeable bases and aluminum, and then washed with distilled water until free from chlorides as indicated by the silver nitrate test. These H-saturated soils were titrated with 0.1N NaOH directly as described above.

Lime Requirement

Lime requirement was determined by the method of Woodruff (63, pp. 53-63) and was also defined as the amount of lime needed to bring the pH of the soil to 6.5 as determined from curves constructed by plotting amounts of lime added against the corresponding pH values. The lime-soil mixtures were incubated for four weeks.

Incubation Procedure

200 gm. of air-dried soil ground to pass a 2 m.m. sieve was

mixed thoroughly with different increments of c.p. calcium hydroxide. The rates added, calculated in tons of calcium carbonate per two million pounds of soil, were dependent upon the cation-exchange capacities of the different soils under investigation. The levels of lime added were from 0 to 45 tons per two million pounds of soil for the coastal soils, i.e. Astoria and Clatsop and from 0 to 8 tons for the Melbourne, Olympic and Willamette soils of the Willamette Valley. This was done in triplicate. Each soil-lime mixture was placed in a 250 ml wide-mouth jar and distilled water was added to bring it to moisture equivalent. The jars were covered with moistened glass wool to prevent contamination and evaporation. These jars were put into a tank filled with water to half the height of the jars. The tank was covered with a moistened linen cloth so that a constant humidity in the tank could be maintained. The samples were in equilibrium with the carbon dioxide in the atmosphere and with the calcium hydroxide in the soils. The moisture lost through evaporation from the linen cloth was restored daily. Samples were taken from the jars at weekly intervals for calcium analysis. This determination was made to ascertain the equilibration between the lime added and the exchange complexes. There was very little difference in the amount of calcium obtained after the first week. At the termination of the fourth week, the soils were air-dried and returned to the original jars.

Soil reaction, exchangeable calcium and exchangeable acidity was determined on all of these soils by the methods previously outlined. From this data calcium and base saturation was obtained.

RESULTS AND DISCUSSION

General Characteristics of the Soils

The results of different chemical analysis on the original soils are given in Table 1. All of the soils are fairly acid as shown by the pH values ranging from 4.7 to 5.7. The two most acid soils are from the coast (Astoria and Clatsop) while the least acid soil is the alluvial soil from the Willamette Valley (Willamette). The two Willamette Valley "red hill" soils (Melbourne and Olympic) are between these extremes.

Organic matter content was much higher in the coastal soils than in the three valley soils. This may be due to higher rainfall and cooler climate. However, these two soils have not been under cultivation to any great extent.

The magnitude of the exchange capacities of the Astoria and Clatsop soils were much greater than those of the other three soils which had low organic matter content. The differences in exchange capacity may have been due to both differences in organic matter and type of inorganic exchange complex. Exchange capacities as determined by the barium chloride buffer method were considerably higher than those determined by the ammonium acetate method. This is in agreement with the observation of other investigators (14, p. 477; 30, pp. 429-445). The relative differences between soils, however, are apparent with both methods.

The amounts of exchangeable calcium vary considerably for

Table 1. Chemical analyses of five western Oregon soils.

Soil	pH	Organic matter per cent	Exchange capacity me./100 gm.	Exchangeable bases			Sodium	Base saturation per cent	Exchangeable aluminum/ me./100 gm.
				Calcium	Magnesium	Potassium			
				me./100 gm.					
				Ammonium Acetate Method			Sodium Acetate		
Astoria	5.0	14.88	42.46	1.5	1.03	0.45	T	7.10	12.52
Clatsop	4.7	12.36	44.85	3.0	5.6	0.70	1.41	23.69	7.42
Melbourne	5.5	4.87	30.37	16.0	5.8	0.77	T	75.10	2.21
Olympic	5.3	5.74	17.77	4.0	1.6	0.23	T	33.11	5.45
Willamette	5.7	3.94	17.89	7.5	2.3	0.83	0	58.93	1.74
				Barium Chloride Method			Lime Requirement ^{2/}		
Astoria			55.4	4.08	1.04	0.12		9.45	5.5
Clatsop			56.8	3.45	4.52	0.18		16.83	7.5
Melbourne			35.6	16.98	4.5	0.47		61.66	2.5
Olympic			23.0	5.65	1.3	0.05		30.43	2.5
Willamette			25.0	10.13	2.6	0.32		52.2	2.5

^{1/} Sodium acetate method. ^{2/} Woodruff method. Tons per acre.

different soils. The low levels of calcium on the coastal soils correspond to the lower pH values but this relation does not hold for all soils. The Melbourne soil contained a considerable amount of exchangeable calcium even though the pH was only 5.5. The relative amounts of exchangeable calcium as determined by the two methods were generally in good agreement for the different soils. The barium chloride buffer method resulted in higher values for exchangeable calcium than did the ammonium acetate method. It cannot be stated whether this difference was due to the extracting solutions or to methods of determining calcium in the solution. It has been shown by Mehlich (31, pp. 289-304), McGeorge (27, pp. 331-336), Puri (50, pp. 165-175), and Marshall (23, pp. 101-199; 24, pp. 1077-1090; 25, pp. 153-165), however, that barium chloride has a stronger power than that of the ammonium acetate for replacing calcium both from the organic and inorganic colloidal fractions having low calcium saturation.

The amount of the exchangeable magnesium varied with the different soils but not to the extent that calcium did. The Clatsop and Melbourne soils contained considerably more magnesium than the other three soils. The Clatsop soil was the only one in which the amount of magnesium was greater than the calcium. When the two methods are compared there is generally good agreement although small deviations are observed in Clatsop and Melbourne soils.

There was less than 1 m.e. of exchangeable potassium per 100 gm. of soil for each of the five soils. The Olympic soil

contained the least amount of potassium. The Astoria soil occurred as the intermediate between the Olympic and the other three. This same tendency can be observed by the two methods. However, the amount of exchangeable potassium as measured by the barium chloride buffer method appears to be much lower than that obtained by the ammonium acetate method. Since the flame photometer was used for the analysis for potassium in both cases, it is difficult to ascertain whether this variation was caused by the flame photometer technique or due to the actual difference in replacing power of the extracting solutions.

The degree of base saturation was quite different in different soils, ranging from 7.1 to 75.1 per cent by the ammonium acetate method and 9.45 to 61.66 per cent by the barium chloride buffer method. This lower degree of base saturation of the coastal soils may be accounted for by the greater extent in leaching under a high rainfall condition. The soil pH and base saturation did not appear to be too closely related since the Clatsop soil had a higher base saturation but lower pH value than that of the Astoria soil. The same thing was true for the Melbourne and Willamette soils.

The amount of exchangeable aluminum in the soils varied considerably ranging from 1.74 m.e./100 gm. in the Willamette soil to 12.52 m.e./100 gm. in the Astoria soil. The colorimetric method used as recommended by Peech (46a, pp. 167-196) is questionable since it is difficult to ascertain whether the aluminum actually

came from the exchange spots of the exchange complexes or from the dissolution of certain amorphous substances which might exist in the soils. However, Peech claimed that the aluminum determined by this procedure was exchangeable.

Comparison of Exchange Capacities as Determined by Different Methods

A comparison of exchange capacities (Table 2) indicate that the barium chloride-buffer method resulted in values approximately 20 per cent greater than those obtained with the ammonium acetate method. It was, therefore, felt to be desirable to use an additional method. The conductimetric titration method proposed by Mortland and Mellor (35, pp. 363-364) was selected.

It has been known that the organic fraction may contribute a large part in the determination of exchange capacity, hence the magnitude of the exchange capacity of the inorganic colloidal fraction may be masked to a great extent owing to the presence of organic matter. The soils were treated repeatedly with 10% hydrogen peroxide as recommended by Truog, et al (60, p. 109) to remove the organic matter so that the exchange capacity due to the inorganic colloidal fraction could be estimated. The results of the exchange capacities of the soils before and after treatment with hydrogen peroxide were performed by the three methods mentioned above (Table 2).

Table 2. Comparison of cation-exchange capacity as determined by different methods before and after the treatment with H_2O_2 .

Soils	Before treatment with hydrogen peroxide*			After treatment with hydrogen peroxide*	
	a	b	c	b	c
	me./100 gm.			me./100 gm.	
Astoria	42.5	55.4	32.0	27.0	16.7
Clatsop	44.9	56.8	34.5	30.0	21.0
Melbourne	30.4	35.6	26.0	20.0	18.0
Olympic	17.8	23.0	17.5	8.6	7.5
Willamette	17.9	25.0	17.5	8.6	7.5

* a = Ammonium acetate method.

b = Barium chloride buffer method.

c = Conductimetric titration method.

Before treatment with hydrogen peroxide. As has been indicated, the differences in magnitude of the exchange capacities between the coastal soils and the valley soils might be partly accounted for by the differences in organic matter content. However, with nearly equal amounts of organic matter in the valley soils, the Melbourne soil had a higher exchange capacity than the other two. This would suggest a higher quantity or difference in type of clay mineral in the Melbourne soil.

The results by the ammonium acetate and the conductimetric titration methods were in good agreement for the valley soils but not for the coastal soils. These were not very consistent with those obtained by Mortland and Mellor (35, pp. 363-364) who worked on certain sandy loam and prairie soils and obtained good agreement between these two methods.

Considerable deviations were observed between the barium chloride buffer and the conductimetric titration methods, with the latter method giving the lowest values. This was most pronounced in the coastal soils.

It has been known that conductivity is entirely due to the ionic dissociation of the salute. The conductivity of a soil suspension free from salt would be entirely due to the dissociation of ions on the surface. Thus, the measurement of conductivities of soils with different exchangeable bases would afford a comparative measure of their degree of dissociation. Relative mobilities of ions in suspension or the different strength of adsorption for

cations by the exchange complexes. Whether the low values of the exchange capacity, as determined by the conductimetric titration, resulted from the relatively low strength of magnesium in replacing barium remains obscure.

After treatment with hydrogen peroxide. After treatment with peroxide the soils became dispersed and sticky, particularly in the Clatsop soil. Olympic and Willamette soils were the least sticky and Astoria and Melbourne soils were intermediate. Consequently, they were extremely difficult to handle during the leaching process on the Buchner funnel with the aid of suction. In such cases the peroxide-treated soils were washed by using successive centrifugation after the samples were treated with leaching solutions. The barium chloride treated soils were washed till free of chloride ions by the silver nitrate test. The acetate ion could not be tested by any ordinary procedure to check on the completeness of washings for ammonium acetate tested soils, hence these results are not presented.

The results of the exchange capacities determinations by the barium chloride-buffer method and the conductimetric titration method were in fairly good agreement in the three valley soils but large deviations still occurred in the coastal soils. The results for the two coastal soils before and after treatment with peroxide seem to suggest that in these soils the lower values obtained by the conductimetric method as compared to those obtained by the barium chloride buffer method were influenced both by the inorganic

and organic fraction. This leads to the hypothesis that there may have been two factors in the coastal soils which might cause the differences in exchange capacity by these two methods. First, some inorganic fractions might have a stronger strength of adsorption for barium than for magnesium. Consequently, the magnesium ions added could not completely replace the barium adsorbed during the titration process. Presumably the nature of the inorganic colloidal fraction was not affected by the treatment with peroxide as indicated by McGeorge (27, pp. 331-336). Second, certain organic fractions might have some specific combination with barium rather than with magnesium and this organic fraction might be resistant to the peroxide oxidation. McGeorge (27, pp. 331-336) reported results for digestion of alfalfa with hydrogen peroxide. A large part of the exchange capacity was not destroyed and he suggested that hydrogen peroxide only partly destroyed the lignin compounds and partially reduced the organic exchange capacity. When the peroxide-treated Astoria and Clatsop soils were leached with barium chloride buffer, some unknown floccule-like precipitate appeared in the leachate which was soluble in HCl and gave a positive test for barium with sulfate. It was not certain whether this precipitate indicated some barium, organic or barium-inorganic colloidal complex. However, Puri (50, pp. 165-175) presented data which showed that the chloride

salts of alkaline earth metals would form humate precipitates within certain pH ranges in the alkaline range.

The conductimetric titration curves for the untreated soils are shown in Figure 1. Before the soils were treated with hydrogen peroxide, three types of slopes were obtained on the first portion of the curves. They are fairly steep in the case of the Willamette and Olympic soils, slightly inclined for the Astoria and flat for the Clatsop and Melbourne soils. The first three curves are different in this respect from those shown by Mortland and Møller (35, pp. 363-364). Any increase in specific conductance as magnesium sulfate was added would suggest that the strength of adsorption for magnesium was less than for barium.

The conductimetric titration curves for the soils after treatment with hydrogen peroxide are shown in Figure 2. The first portion of the curves all become flat. This suggests that the strength of adsorption for magnesium by the exchange complexes was increased with the peroxide treatment.

If one assumes that only the organic fraction influences the slope of the curves, then the slopes should become zero after treatment with peroxide. The fact that the Melbourne and Clatsop soils did not have a positive slope prior to treatment with peroxide would indicate that organic matter was not the only factor to influence the slope of the titration curve unless the type of organic matter was much different in the soils.

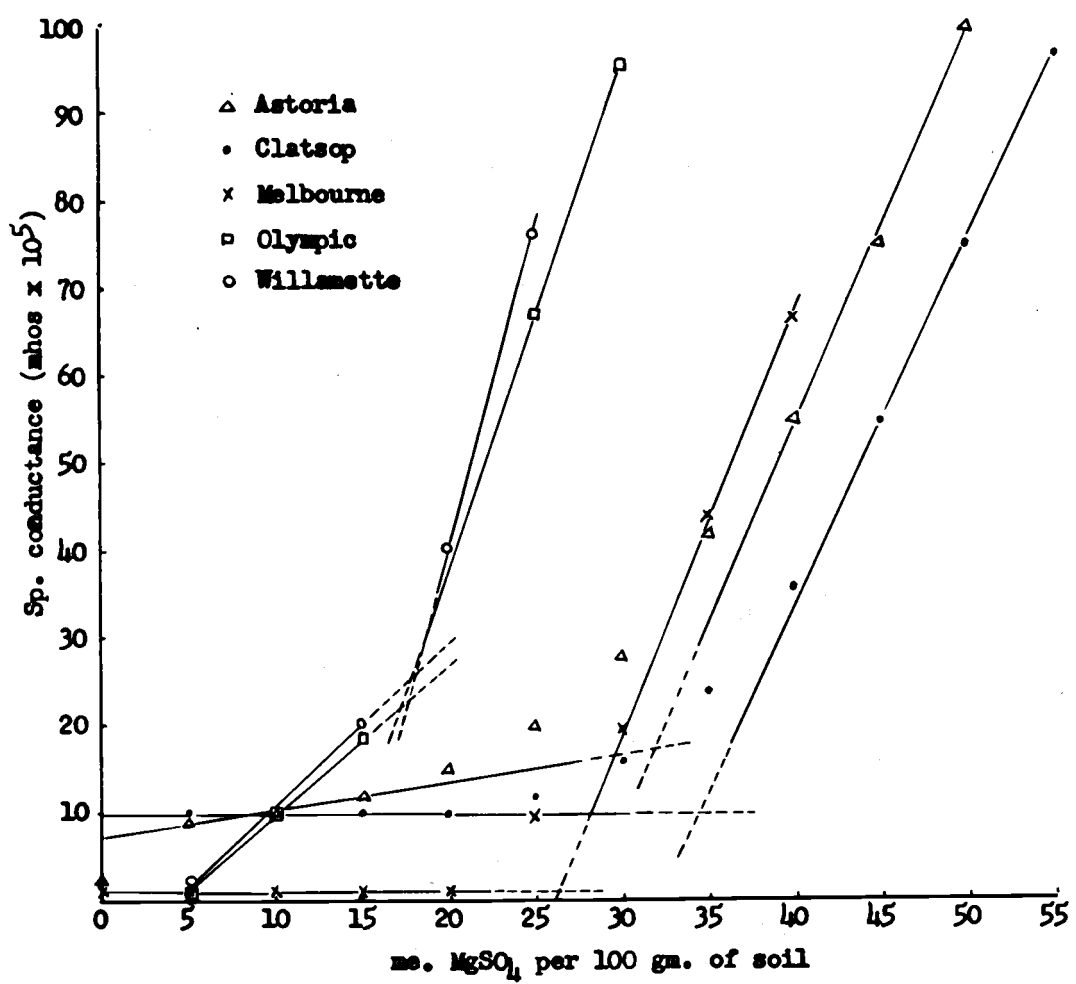


Figure 1 . Conductimetric titration curves for barium-saturated untreated soils.

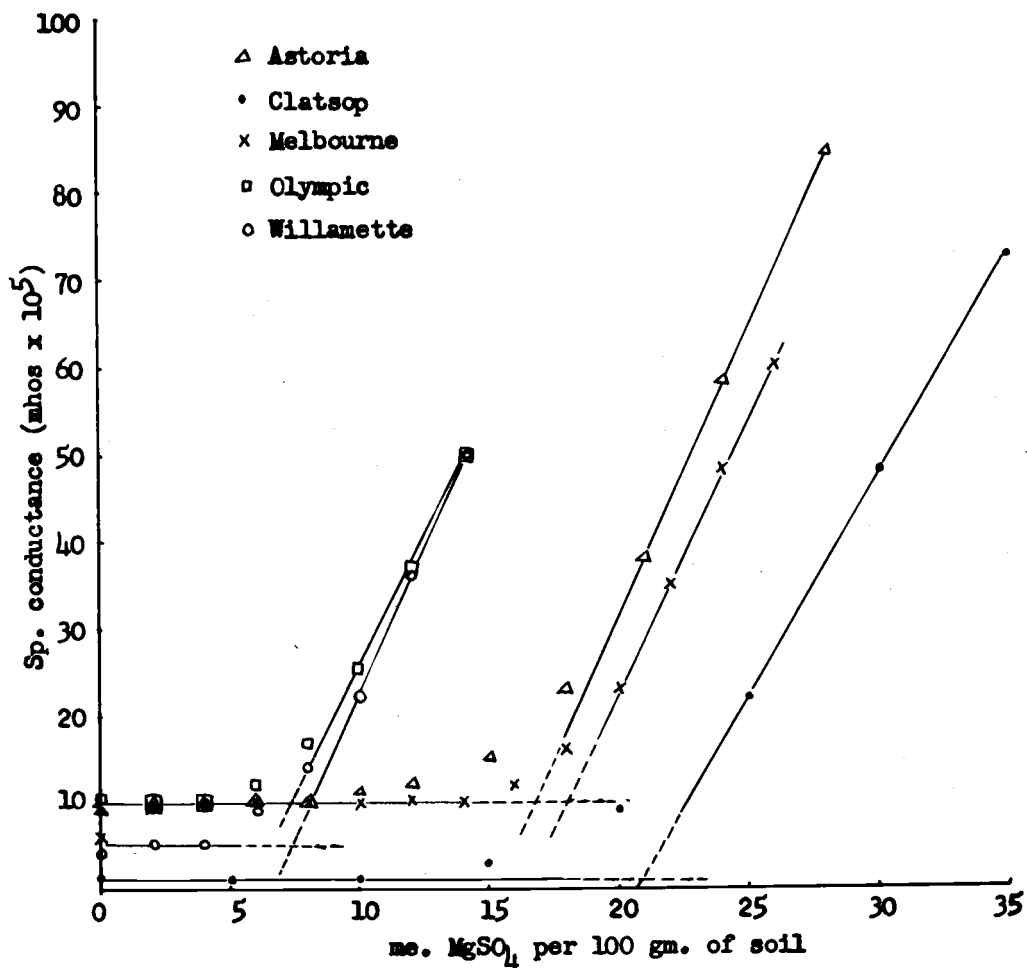


Figure 2 . Conductimetric titration curves for barium-saturated soils treated with hydrogen peroxide.

The results in magnitudes of exchange capacity and the slopes of the curves for the soils before and after treatment with peroxide lead to the further speculation that the inorganic colloidal fraction in the coastal soils are quite different from the Olympic and Willamette soils. The Melbourne soil appears to be more closely related to the coastal soils in this respect.

The Nature of the Buffering Properties

In order to study the nature of the buffering properties of the soils, potentiometric titrations were made on each soil before and after leaching with HCl. The soils were titrated directly with 0.1 N sodium hydroxide and the pH values were noted with each addition of base after five minutes stirring.

Potentiometric titration curves for the original soils. The curves for the untreated soils are shown in Figure 3a. The curves for the two coastal soils are quite similar and show fairly well-buffered properties over the complete pH range. No sharp inflections or end points were observed on either of these two soils. This type of buffering characteristic may be associated with soils having a greater amount of organic matter. However, Mehlich indicated that montmorillonite clay would show similar buffering characteristics as did a peat (29, p. 50). The three valley soils exhibit similar buffering properties between themselves with their curves rising rapidly indicating slight buffering properties. No

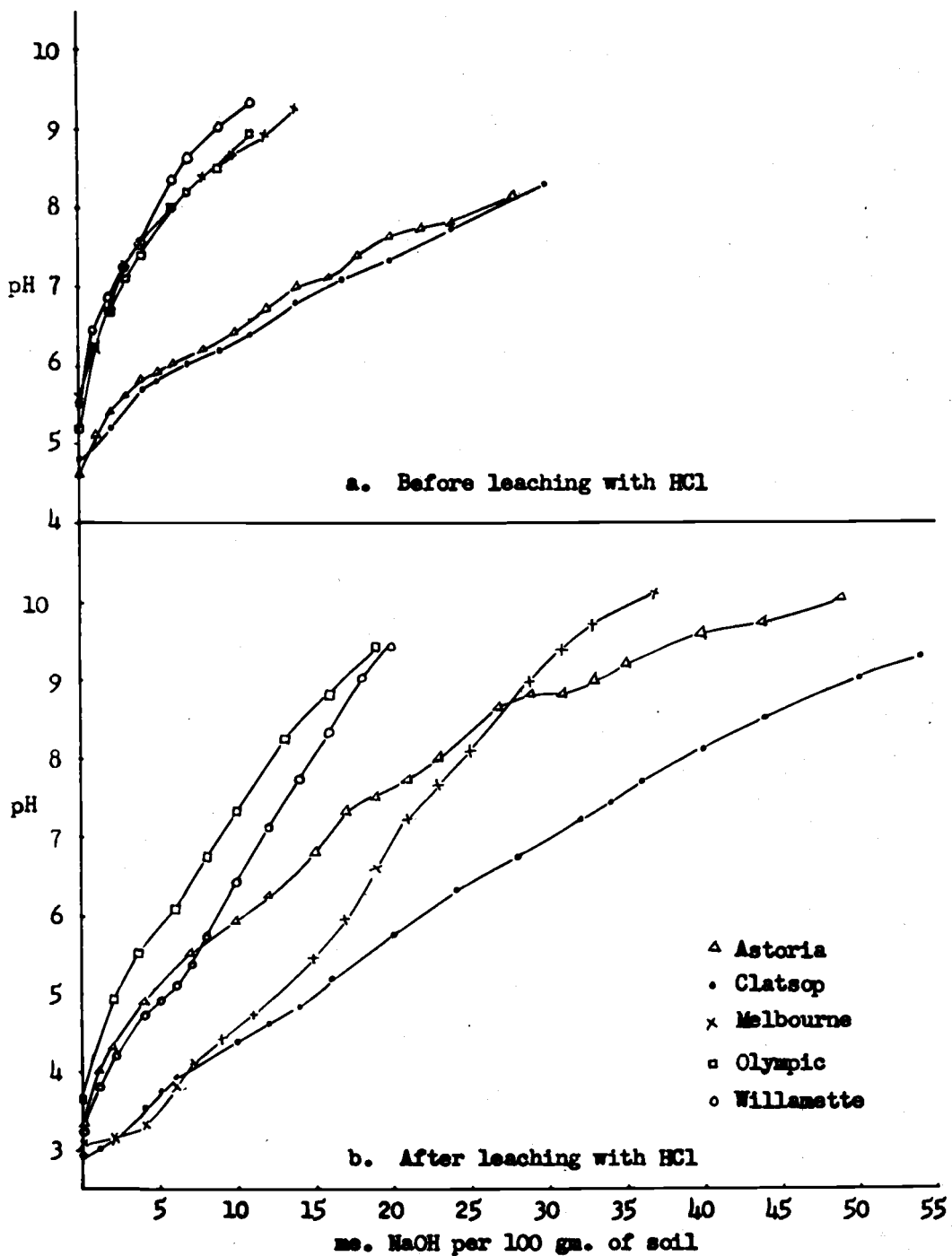


Figure 3 . Potentiometric titration curves of soils before and after leaching with 1N HCl.

sharp inflections were observed on any of the soils either.

Potentiometric titration curves for soils leached with HCl.

Each soil was leached with N HCl in order to remove the exchangeable bases and aluminum. These "hydrogen-saturated" soils were titrated directly as soon as possible, otherwise the hydrogen would exchange for aluminum from the crystal lattice of the clay mineral present in the soil and an aluminum predominating soil instead of hydrogen-saturated soil would result (15, pp. 181-188; 24, pp. 1077-1090).

In Figure 3b, the slope of the curves for the Olympic soil still remained the same as before leaching with HCl, being slightly buffered through the whole pH range. The curve for the Willamette soil is indicative of slight buffering around pH 5 and then rises rapidly in almost a straight line. However, the position of the curves for these two soils were lowered and reversed. It would be expected that the change in position of the curves was due to the replacement of exchangeable bases already present by hydrogen. The Willamette soil had a higher degree of base saturation prior to treatment with HCl thus accounting for its lower position. No strong acid properties were indicated from the curves for the Olympic and Willamette soils, suggesting that exchangeable aluminum was not replaced by hydrogen or that these soils may contain 1:1 type clay minerals in which hydrogen is relatively strongly adsorbed (24, pp. 1077-1090).

In the case of the Melbourne soil, the position of the curve was lower after treatment with HCl to a greater extent than those of the Olympic and Willamette soils. This variation in the curve before and after leaching with HCl might be due to the fact that the Melbourne soil had the highest degree of base saturation among the five soils. It might also suggest a possibility that the type and amount of clay mineral in the Melbourne soil was different from those in the Olympic and Willamette soils. On the other hand, the slope of the curve has also been changed and it exhibits a strong acid property, being buffered somewhat between pH 3 to 4. There was also some indication of weak acid properties, being slightly buffered between pH 4.5 and 5.5.

The curve of the Astoria soil was situated intermediately between those of the Olympic and Melbourne soils and shows slight buffering between pH 3.5 and 5.5. This initial inflection followed by further buffering may be attributed to the presence of aluminum (15, pp. 181-188; 22, pp. 135-139). The shape and position of this curve seemed to be little affected by leaching with HCl although the initial pH was lowered somewhat. This was probably due to the fact that the Astoria soil had the lowest degree of base saturation among the five soils.

The curve for the Clatsop soil was situated at the lowest position of the five curves but the slope remained practically the same after leaching as before. The shape of the curve indicates a slight buffering characteristic at pH 3 to 4 and then rises gradually in nearly a straight line, indicating a fairly well buffered characteristic. The weak acid property of the curve for the Clatsop soil suggests that no aluminum was replaced by hydrogen after leaching with HCl.

The shape of the curves indicates that the Melbourne soil was the only one which exhibited the replacement of some exchangeable aluminum by hydrogen. These observations seem to be contradictory with the results of the quantity of aluminum obtained by the procedure recommended by Peech (46a, pp. 167-196) (Table). The latter indicated that high amounts of exchangeable aluminum were present in Astoria and Clatsop soils but a small amount in the Melbourne soil. This leads one to speculate that some amorphous substance was present in the coastal soils and that the exchangeable aluminum referred to by Peech was not necessarily the case.

Effect of Additions of Lime on the Exchange Properties of the Soils

The pH values, exchangeable acidity, degree of calcium saturations, degree of base saturation and the sum of the exchangeable cations for the five soils resulting from the additions of lime as determined by the ammonium acetate and the BaCl_2 -buffer methods are given in Tables 3 to 7.

It was interesting to note that the pH values of all the unlimed soils (i.e. 0 ton per acre) were all lower than those of the original soils listed in Table 1. Since these unlimed soils have been incubated along with the limed samples for four weeks, it is possible that the decrease in pH was due to microorganism activity under the optimum temperature and moisture conditions.

As would be expected, the pH increased and exchangeable acidity decreased with each addition of lime for all samples. However, in all soils some acidity still remained unneutralized even above pH 7 when measured by the BaCl_2 buffer method. The amounts of acidity obtained by subtracting the exchangeable bases from the exchange capacity, as determined by the NH_4OAC method, are much lower than those measured by the BaCl_2 -buffer method. These results are consistent with those obtained by Shaw (55, pp. 437-451) and Mehlich (30, pp. 429-445; 31, pp. 289-304; 32, pp. 162-166) indicating the inability of ammonium acetate to replace hydrogen completely.

The amount of exchangeable calcium increases with additions of lime as would be expected. There appears to be little difference in the two methods used for the determination of the amount of calcium adsorbed by the soils except in the case of the Astoria and Clatsop soils where the amount of lime added exceeds the exchange capacity of these two soils.

The data in Table 3 indicate that 25 tons of lime added to the Astoria soil is more than enough to obtain complete calcium and

Table 3. Effect of additions of lime on the exchange properties of Astoria soil.

Amount of lime added Tons/Acre	pH	Exchangeable acidity ^{1/}		Exchangeable calcium		Calcium saturation		Base saturation		Sum of exchange- able cations ^{2/}
		a ^{1/}	b ^{1/}	a	b	a	b	a	b	b
		me./100 gm.		me./100 gm.		per cent		per cent		me./100 gm.
0	4.6	39.48	51.06	1.5	4.08	3.57	7.36	7.10	9.45	56.30
3	4.9	34.52	46.84	6.46	8.72	15.38	15.74	18.90	17.83	56.72
6	5.1	28.64	42.62	12.34	13.11	29.38	23.66	32.90	25.76	56.89
8	5.3	24.98	39.67	16.00	16.82	38.10	30.36	41.62	32.45	57.65
10	5.6	22.89	37.14	18.09	19.28	43.07	34.80	46.60	36.90	57.56
14	6.1	14.85	28.70	26.13	27.01	62.21	48.75	65.74	50.85	56.87
20	6.6	6.81	18.57	34.17	33.44	81.36	60.36	84.88	62.45	53.17
22	7.3	1.98	16.88	39.00	36.16	92.86	65.27	96.38	67.36	54.20
25	7.5		13.50	44.92	41.38	106.95	74.69	110.48	76.79	56.05
30	7.6		9.30	49.07	49.53	115.57	89.40	119.05	91.50	59.99
35	7.9		4.23	55.14	55.18	129.86	99.60	133.35	101.70	60.57
45	8.3		-2.96	64.95	60.60	152.97	109.39	156.45	111.48	

^{1/} a. Ammonium acetate method; b. barium chloride buffer method.
^{2/} Magnesium, potassium and sodium taken from Table 1.

Table 4. Effect of additions of lime on the exchange properties of the Clatsop soil.

Amount of lime added Tons/Acre	pH	Exchangeable acidity		Exchangeable calcium		Calcium saturation		Base saturation		Sum of exchange- able cations ^{2/} me./100 gm.
		a ^{1/} me./100 gm.	b ^{1/} me./100 gm.	a me./100 gm.	b me./100 gm.	a per cent	b per cent	a per cent	b per cent	
0	4.4	34.14	41.25	3.0	3.45	6.67	6.07	23.69	16.83	50.81
3	4.6	28.01	38.82	9.13	8.88	20.29	15.63	37.31	26.39	53.81
6	4.9	20.60	31.65	16.54	15.62	36.76	27.50	53.78	38.26	53.38
8	5.1	18.39	29.54	18.75	16.98	41.67	29.89	58.69	40.65	52.63
10	5.3	14.64	27.01	22.50	19.80	50.00	34.84	67.03	45.62	52.92
14	6.0	6.51	20.68	30.63	27.94	68.07	49.19	85.09	59.95	54.73
20	6.7		12.66	37.33	37.09	82.96	65.30	100.42	76.05	55.86
22	6.9		10.13	40.16	41.27	89.24	72.66	106.27	83.42	57.51
25	7.5		6.33	46.33	47.59	102.96	83.79	119.98	94.54	60.03
30	7.6		0.40	50.90	54.34	113.49	95.67	130.68	106.43	60.49
35	7.8		-0.80	57.72	58.06	128.70	102.22	145.89	112.98	
45	8.0		-2.54	73.62	60.08	164.15	105.77	181.34	116.53	

^{1/} a. Ammonium acetate method; b. Barium chloride buffer method.
^{2/} Magnesium, potassium and sodium taken from Table 1.

Table 5. Effect of additions of lime on the exchange properties of the Melbourne soil.

Amount of lime added Tons/Acre	pH	Exchangeable acidity		Exchangeable calcium		Calcium saturation		Base saturation		Sum of exchange-
		a ^{1/} me./100 gm.	b ^{1/} gm.	a	b	a	b	a	b	able cations ^{2/} me./100 gm.
0	5.3	7.80	16.12	16.00	16.98	52.50	47.70	75.10	61.66	38.07
0.5	5.5	6.80	15.34	17.00	18.03	56.67	50.65	78.40	64.61	38.34
1.0	5.8	6.25	14.01	17.55	18.80	58.50	52.81	80.23	66.77	37.78
1.5	6.0	4.80	12.33	19.00	20.38	63.33	57.25	85.07	71.21	37.67
2.0	6.1	3.42	11.45	20.38	20.90	67.93	58.71	89.67	72.67	37.32
3.0	6.4	1.42	11.02	22.38	22.68	74.60	63.71	96.33	77.67	38.67
4.0	6.7		9.73	24.08	23.77	80.27	66.77	102.00	80.73	38.47
6.0	7.2		5.84	27.17	27.77	90.57	78.00	112.30	91.97	38.58
8.0	7.5		4.23	31.25	30.43	104.17	85.48	125.9	99.44	39.63

^{1/} a. Ammonium acetate method; b. Barium chloride buffer method.

^{2/} Magnesium, potassium and sodium taken from Table 1.

Table 6. Effect of addition of lime on the exchange properties of the Olympic soil.

Amount of lime added Tons/Acre	pH	Exchangeable acidity		Exchangeable calcium		Calcium saturation		Base saturation		Sum of exchange-
		a ^{1/} me./100 gm.	b ^{1/} gm.	a	b	a	b	a	b	able cations ^{2/} me./100 gm.
0	5.3	11.94	20.26	4.00	5.65	22.22	24.57	33.11	30.43	27.26
0.5	5.3	11.11	17.72	4.83	6.32	26.83	27.48	37.70	33.35	25.39
1.0	5.4	10.19	16.88	5.75	7.00	31.94	30.43	42.88	36.30	25.23
1.5	5.5	9.44	16.04	6.50	7.63	36.11	33.17	47.10	39.04	25.02
2.0	5.6	8.69	14.35	7.25	8.26	40.28	35.91	51.32	41.78	23.96
3.0	6.0	7.19	13.92	8.75	9.25	48.61	40.22	59.76	46.09	24.52
4.0	6.4	5.77	10.97	10.17	11.55	56.50	50.22	67.75	56.09	23.87
6.0	6.9	1.27	9.28	14.67	14.11	81.50	61.35	93.08	67.22	24.74
8.0	7.2		5.48	17.75	18.03	98.61	78.39	110.41	84.26	24.83

^{1/} a. Ammonium acetate method; b. Barium chloride buffer method.

^{2/} Magnesium, potassium and sodium taken from Table 1.

Table 7. Effect of additions of lime on the exchange properties of Willamette soil.

Amount of lime added Tons/Acre	pH	Exchangeable acidity		Exchangeable calcium		Calcium saturation		Base saturation		Sum of exchange- able cations ^{2/}
		a ^{1/} me./100 gm.	b ^{1/} me./100 gm.	a me./100 gm.	b me./100 gm.	a per cent	b per cent	a per cent	b per cent	b me./100 gm.
0	5.3	7.26	13.92	7.50	10.13	41.67	40.52	58.93	52.20	26.97
0.5	5.5	6.01	13.50	8.75	10.45	48.61	41.80	65.78	53.48	23.87
1.0	5.7	5.38	12.66	9.38	10.45	52.11	41.80	69.28	53.48	26.03
1.5	5.9	4.03	11.39	10.73	11.54	57.61	46.16	74.78	57.84	25.85
2.0	6.1	4.51	10.34	11.25	11.76	62.50	47.04	79.67	58.72	25.02
3.0	6.4	2.26	8.86	12.50	13.85	69.44	55.40	86.61	67.08	25.63
4.0	6.7	0.26	7.17	14.50	14.63	80.56	58.52	97.72	70.20	24.72
6.0	7.1		5.48	18.17	17.76	100.94	71.04	118.11	82.72	26.16
8.0	7.4		2.95	22.25	21.42	123.61	85.68	140.88	97.36	27.29

^{1/} a. Ammonium acetate method; b. Barium chloride buffer method.

^{2/} Magnesium, potassium and sodium taken from Table 1.

base saturation by the ammonium acetate method. However, 100 per cent calcium and base saturation could not be obtained when determined by the barium-chloride buffer method, until more than 35 tons of lime were added. In the Clatsop soil (Table 4) between 25 and 30 tons of lime is required to completely saturate this soil when determined by BaCl_2 -buffer method but 20 tons is enough by the ammonium acetate method. Considerable differences in the degrees of calcium and base saturation in the three valley soils can also be observed between the two methods used. For example, 104 per cent calcium-saturation and 126 per cent base saturation were obtained by the ammonium acetate method and only 85 per cent calcium-saturation and 99 per cent base saturation by the BaCl_2 -buffer method when 8 tons of lime were added to the Melbourne soil. The same tendency occurred in the other two soils except that much more lime was required to completely saturate the Olympic soil when determined by the BaCl_2 -buffer method.

It would be expected that the differences in amount of lime required to bring a soil to 100 per cent calcium and base saturation might be associated with the exchange capacity and the corresponding degree of base saturation of the soil. For example, the Astoria and Clatsop soils had similar exchange capacities by both methods but the Astoria soil had the lowest degree of base saturation; consequently, the Astoria soil required more lime than the Clatsop to obtain 100 per cent base saturation for the Clatsop soil. The same thing was true for the Olympic and Willamette soils.

The Melbourne soil had both a higher exchange capacity and degree of base saturation than the Olympic and Willamette soils; therefore, required less amount of lime to obtain a 100 per cent base saturation. When the coastal soils and the valley soils were compared, it can be observed that the former required approximately 2 to 3 times as much lime as that in the latter to obtain complete base saturation. This is due to the fact that the coastal soils had higher exchange capacities but lower degree of base saturation than those for the valley soils.

The sums of the exchangeable cations in the last column of Table 3 to 8 are obtained by adding the exchange acidity to the exchangeable bases, i.e., magnesium, calcium, potassium and sodium, from Table 1. All of these cations are measured by the same barium chloride-buffer procedure. In Tables 3, 5, 6, and 7 the sums of the exchangeable cations for the Astoria, Melbourne, Olympic and Willamette soils are fairly constant and about 2 to 3 me. higher than the values of the corresponding exchange capacities (Table 1). However, a peculiar phenomena occurred in the Clatsop soil. The sum of the exchangeable cations increased with the first addition of lime and remained somewhat lower than the value of the exchange capacity until 22 tons of lime were added. At this point (pH 6.0) the sum of exchangeable cations again increased until they were 2 to 3 me. above the exchange capacity similar to the other four soils.

It is possible that the first increase in the sum of the

exchangeable cations in the Clatsop soil was due to the low level of microorganism activity in the original soil brought about by the wet, acid condition under which it developed. The lower values in the sums of the exchangeable cations in the Clatsop soil between pH 4.6 and 6.0 might be due to either the incomplete replacement of calcium or the incomplete replacement of soil acidity during the leaching process. Since the amounts of the exchangeable calcium as determined by both methods were fairly consistent and the changes in exchangeable calcium was greater than those of the corresponding changes in acidity with each addition of lime, it is more likely that this lower value in the sums of the exchangeable cations was due to the low values of the acidity resulting from the incomplete neutralization during leaching. This could easily be brought about because the lighter texture of the Clatsop soil allowed the extraction solution to pass through more rapidly than in the other four soils.

The values of the sum of exchangeable cations that are higher than the exchange capacities for the four other soils, as well as the Clatsop, may be explained on the basis of the extra acidity produced through microorganism activity during the incubation period under optimum conditions.

It has been reported by Throm and Smith (58, pp. 392-396) that the general level of microorganism activities in limed plates which were at the neutral point were about 2 to 3 times that of acid plates which contained acid soils between pH 3.9 and 4.4.

This increase in acidity may have dissolved some of the lime added giving rise to higher levels of exchangeable calcium. This has been proposed by Shaw (56, pp. 421-443).

A comparison of the effect of the two extracting solutions upon the calcium replaced from the Astoria and Clatsop soils is shown graphically in Figure 4. It can be observed from the curves that the calcium replaced by the BaCl_2 -buffer approaches a relatively constant amount of around 55-60 me. with the higher additions of lime. These points indicate saturation points and are fairly consistent with the magnitudes of the exchange capacity as measured by BaCl_2 -buffer method. The amounts of calcium replaced by ammonium acetate increases with the additions of lime regardless of the saturation point. This observation, previously demonstrated by Mehlich (31, pp. 289-304) clearly indicates that ammonium acetate can not only replace all the exchangeable calcium but also dissolves some free calcium carbonate present in soils. Thus, the reason that the sum of exchangeable cations may exceed the exchange capacity in soils containing free carbonates may be entirely due to the fact that ammonium acetate dissolves some free carbonates.

The Relationship between pH and Base Saturation

The relationship between pH and base saturation as determined by the two methods is shown in Figures 5 and 6. The shape of the curves varied with different soils and the variation appeared to be

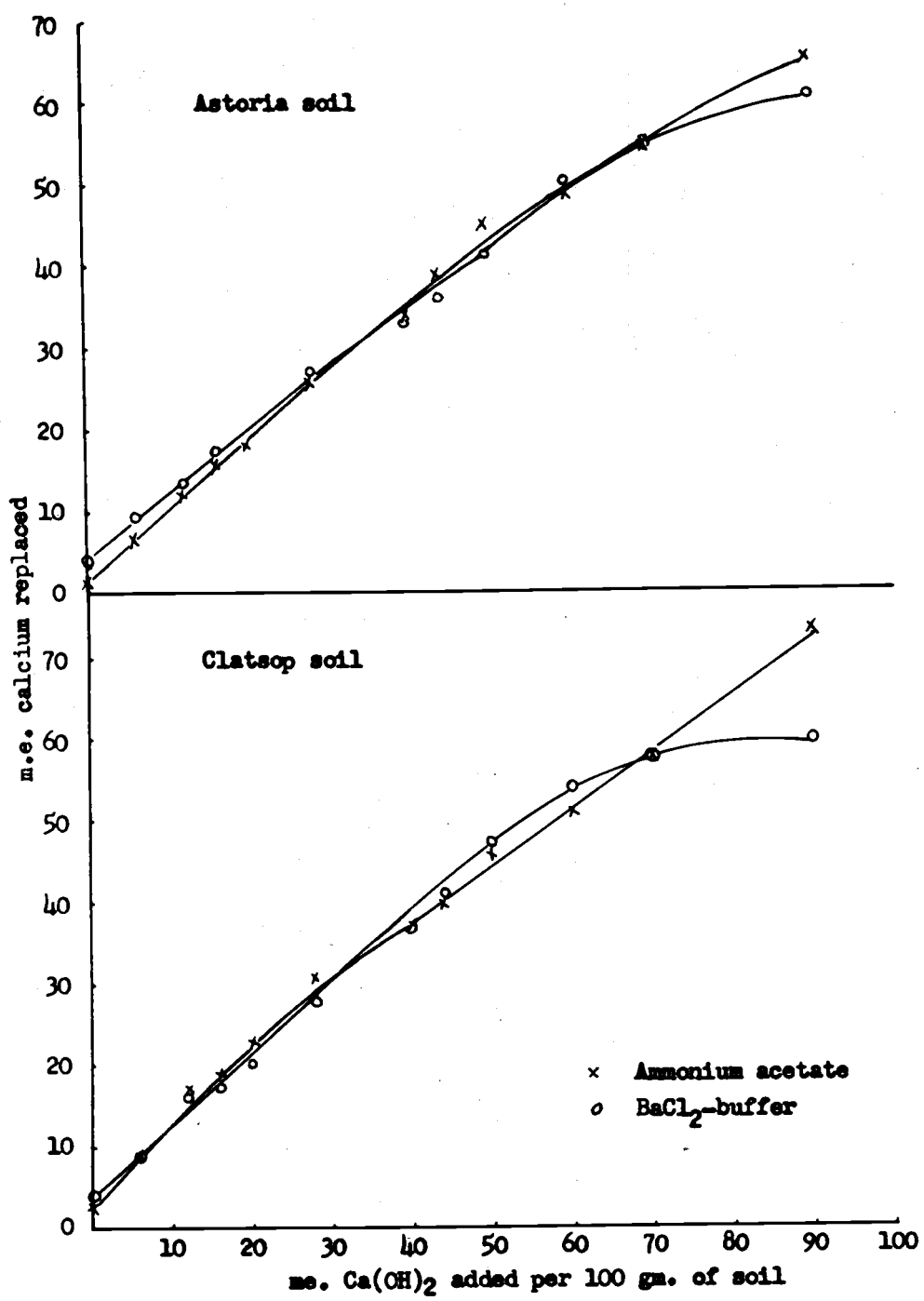


Figure 4 . Effect of extracting solutions on amount of calcium replaced from Astoria and Clatsop soils.

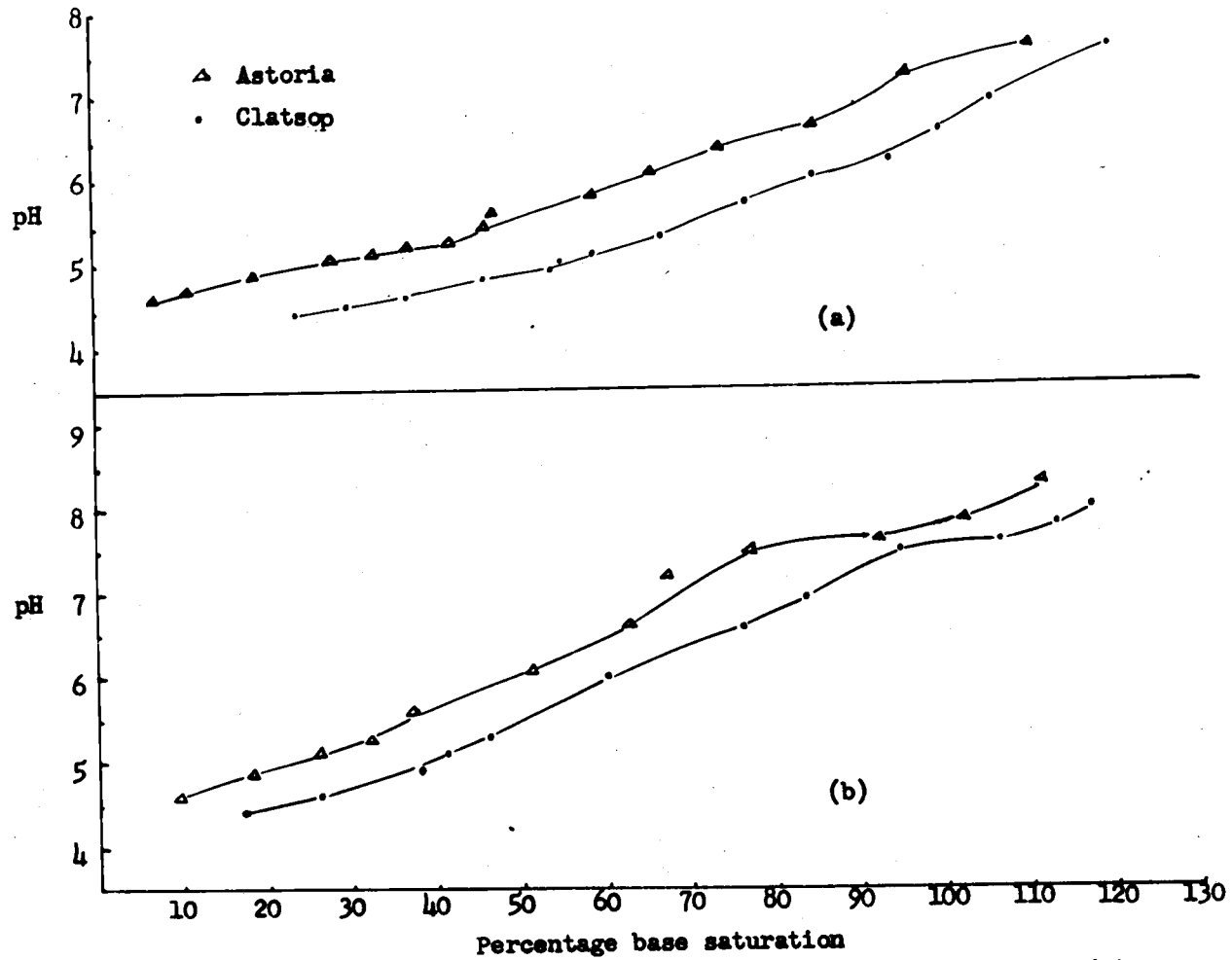


Figure 5. Relationship between pH and base saturation as determined by (a) ammonium acetate and (b) BaCl₂-buffer methods on the coastal soils.

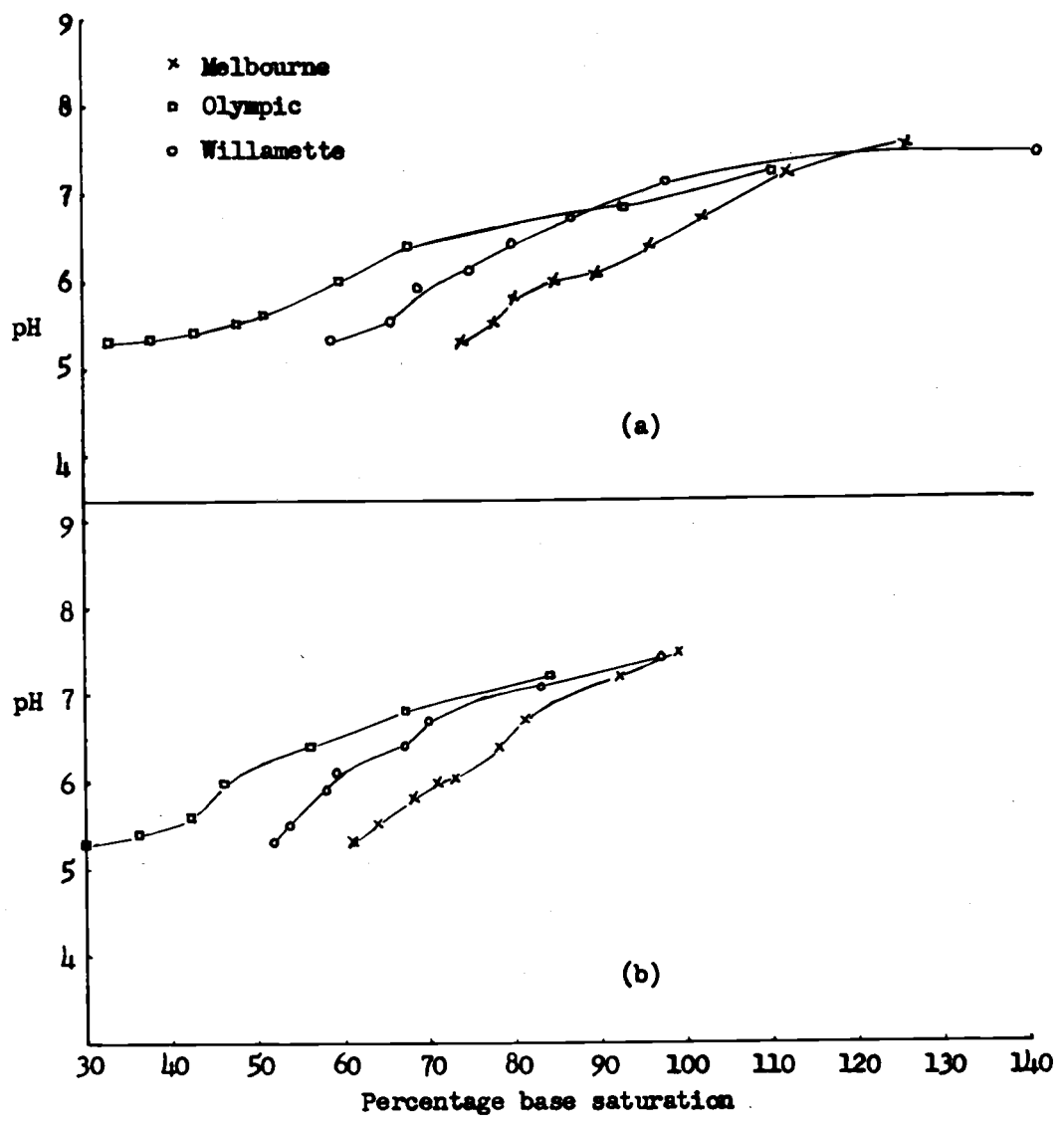


Figure 6 . Relationship between pH and base saturation as determined by (a) ammonium acetate and (b) BaCl₂-buffer methods on the valley soils.

more pronounced between the coastal soils (Figure 5) and the valley soils (Figure 6) no matter which method was used. In the coastal soils there was a parallel linear relationship between the pH values and the base saturation up to 100 per cent by the ammonium acetate method while this relationship held only up to 80 to 90 per cent base saturation by the barium chloride buffer method. However, the slope of the parallel linear portion of the curves obtained by the BaCl_2 -buffer method is steeper than those obtained by the ammonium acetate method.

In the three valley soils inflection points occurred at 55, 70 and 85 per cent base saturation for the Olympic, Willamette, and Melbourne soils respectively, when the ammonium acetate method was used, and at 45, 60 and 75 per cent when the barium chloride buffer method was used. The lower portions of the curves seemed to be somewhat parallel but approached a common end-point as the per cent base saturation increased. This same feature was observed when both methods were used. However, the slopes of the curves were greater in the case of the barium chloride method than for the ammonium acetate method.

Mehlich (29, p. 50) has suggested that although the buffer properties and base exchange capacities for different soils differ markedly, the base saturation-pH relationship is not affected by these differences. He also pointed out that this relationship could be subject to error if such colloidal factors as silica, aluminum and iron oxides were present in the system and the presence

of organic matter might modify this relationship. It is possible that the differences in the type of curves between the coastal soils and the three valley soils were due to the organic matter content and the differences in type of clay minerals present.

The percentages of base saturation are quite different for the different soils at any given pH value. These differences in base saturation appear to be more pronounced in the coastal soils than with the other three. In order to compare the degrees of base saturation, pH 7 was taken as an arbitrary value. Thus, the degree of base saturation in percentage as measured by the two methods at pH 7.0 for the five soils studied are as follows:

<u>Soil type</u>	<u>Ammonium acetate method per cent</u>	<u>BaCl₂-buffer method per cent</u>
Astoria	93	69
Clatsop	108	85
Melbourne	108	87
Olympic	100	75
Willamette	95	78

As indicated by Mehlich (29, p. 50) organic matter and 2:1 type clay minerals were almost completely neutralized at pH 7.0 to 7.4 and only 50 to 80 per cent neutralization could be obtained for 1:1 type clay minerals at these same pH values. From the degree of base saturation obtained by the barium chloride buffer method listed above there were some indications that the type of

clay minerals in the Clatsop and Melbourne soils were similar to the 2:1 type and the other three were similar to the 1:1 type. However, from the magnitude of exchange capacity obtained by the different methods before and after treatment with peroxide (Table 2) and the potentiometric titration curves (Figure 3), the Astoria soil seemed to contain 2:1 type clay. Whether the observation noted from the pH-base saturation relationship indicated above was influenced by organic matter or by some amorphous substance was not ascertained.

Pratt and Halowaychuk (49, pp. 365-368) stated that if the concept of base saturation as defined by Bradfield and Allison (4, pp. 8-15) is used in the study of soil, the pH value for 100 per cent base saturation with calcium being the dominant ion in the exchange complex, is usually between 7.6 and 8.2 for most soil samples. The degree of base saturation as determined by the ammonium acetate method for these five soils were one hundred per cent at a pH between 6.5 to 7.0. By the barium chloride method the pH values at 100 per cent base saturation are close to 7.5 or higher. If this definition is used, the barium chloride buffer method gives better agreement than the ammonium acetate method.

Figure 7 shows the relationship between the percentage of base saturation and the amount of lime added. A greater amount of lime is necessary to obtain a given increase in base saturation for the two coastal soils than for the valley soils. This is in good agreement with the fact that the coastal soils have higher

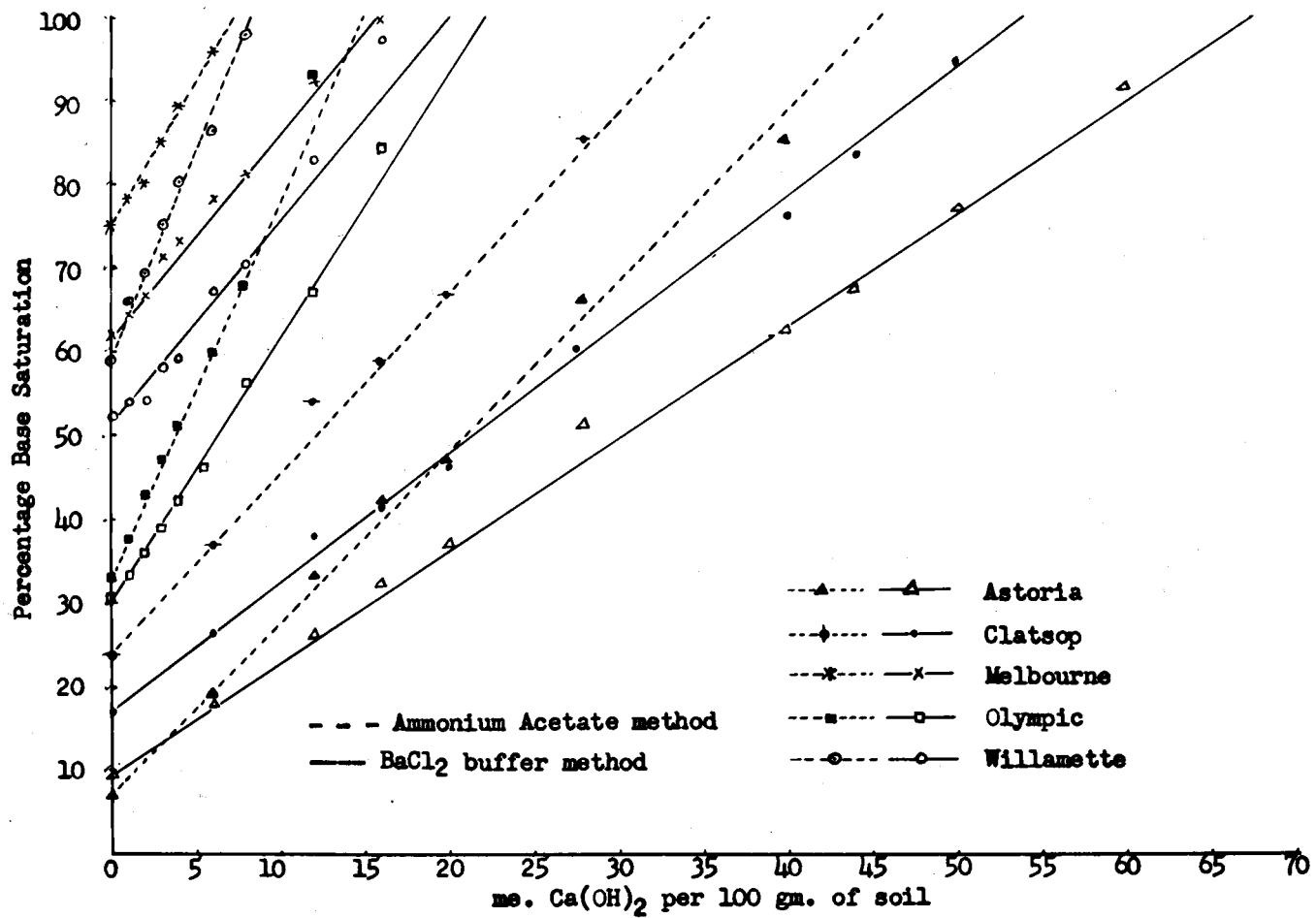


Figure 7. Relationship between lime added and base saturation as determined by the ammonium acetate and the BaCl₂-buffer methods.

exchange capacities and lower base saturation percentages than do the valley soils. As also seen from these curves, the amount of lime necessary to bring any given soil up to a desired base saturation will depend upon the method used since the slopes of the curves are different for the two methods. In all cases, it takes a larger quantity of lime to obtain a given degree of saturation when the exchange capacity and the exchangeable calcium are determined by the barium chloride buffer method.

Lime Requirement

From the standpoint of practical application, the term "lime requirement" should be defined as the amount of lime which is required to bring the soil reaction to such a condition that maximum crop production can be obtained. Naturally this amount of lime required may vary with different species of plants grown. However, pH 6.5 is generally considered to be the optimum value for most crops. For laboratory purposes the lime requirement has been arbitrarily defined by Woodruff (63, pp. 53-63) as the amount of lime required to rise the pH of soil to pH 7.0. It is recognized, however, that the actual pH value observed in the field will be in the neighborhood of 6.5.

The pH-lime relationship as obtained by the incubation procedure is shown in Figure 8. From the curves for the valley soils it is noted that the amounts of lime required to bring the soils to a given pH were inversely proportional to the degree of base

saturation, but the opposite was observed for the coastal soils. There is a great difference in the amount of lime needed to raise the soil pH to any desired level in the coastal soils as compared to the valley soils. It is quite likely that both organic matter and type of clay minerals are responsible for this.

The amounts of lime which was added to the various soils to raise the pH to 6.5 by the incubation procedure (Figure 8) and those by the Woodruff method (Table 1) are compared as follows:

	<u>Woodruff's Method</u> Tons/Acre	<u>Incubation Method</u> Tons/Acre
Astoria	5.5	17.0
Clatsop	7.5	18.0
Melbourne	2.5	3.0
Olympic	3.0	4.0
Willamette	2.5	3.0

The results indicate that good agreement is obtained by the two methods in the three valley soils, but not in the Astoria and Clatsop soils. From the nature of the potentiometric titration curves before leaching with HCl (Figure 3a) and from the amounts of acidity as determined by the barium chloride buffer method (Tables 3 and 4), it seems quite evident that these two soils would require as much lime as estimated by the incubation procedure to neutralize the soil acidity. As seen from the results in Tables 3 to 7, the soil

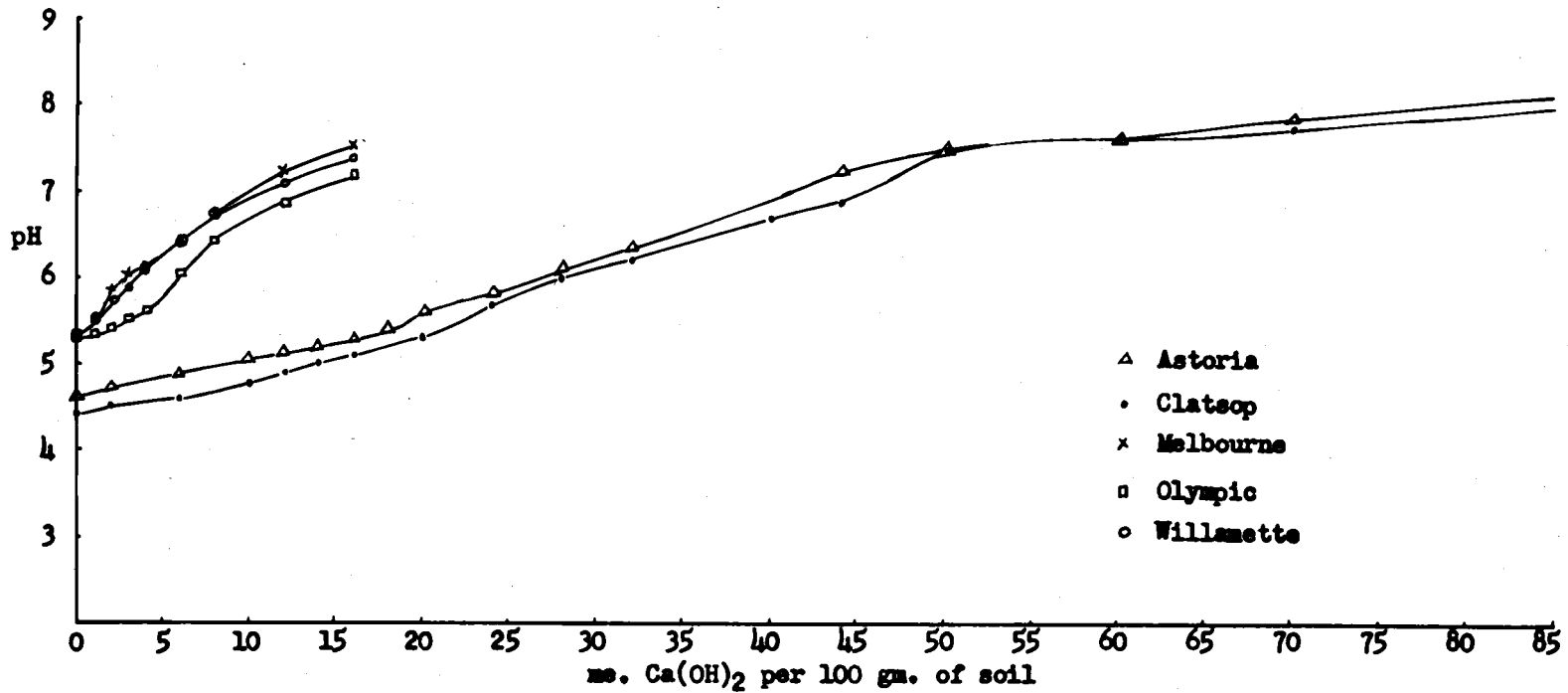


Figure 8 . Effects of increments of lime on pH after four weeks of incubation of field capacity.

acidity determined by the barium chloride buffer method cannot be neutralized completely even at pH 7. It would seem, therefore, that the buffer solution at pH 7 recommended by Woodruff is not strong enough to neutralize the acidity completely on the coastal soils thus accounting for the low values in the lime requirement. It is further evident from the base saturation-lime relationship curves shown in Figure 7 that the amount of lime predicted by the Woodruff procedure would not be enough to bring the coastal soils to 75 or 80 per cent base saturation no matter which method might be used for the determination of the base saturation.

More investigations concerning the chemical characteristics of both organic and inorganic exchange complexes are needed in order to clarify the soil acidity problems on the coastal soils. It should be emphasized also that from the viewpoint of crop production it is questionable whether 17 to 18 tons of lime may be necessary to obtain the maximum production. Laboratory, greenhouse and field work will be required to solve this question. If the base saturation is used as the criteria for lime requirement, the method used both for the determination of exchange capacity and the exchangeable calcium should be specified.

Abnormal Properties Found in the Coastal Soils

Even though the coastal soils are much different from the valley soils, yet there were certain properties exhibited by them which seemed to be abnormal.

The value of the exchange capacities for these soils were different with each of the methods used whether or not the organic matter was destroyed.

Reproducible results for exchange capacity for the Astoria soil could not be obtained when BaCl_2 -buffer was used, the values ranging from 50 me. to 60 me. per 100 gm. Values from 37 me. to 42 me. per 100 gm. were obtained by the ammonium acetate method.

The potentiometric titration curves for these soils were different depending upon whether the soils were titrated serially after standing 48 hours or titrated directly within a few hours.

The weak acid properties shown in the potentiometric titration curves, after leaching with HCl, suggest that no exchangeable aluminum had been replaced by hydrogen. However, high amounts of exchangeable aluminum had been obtained by the chemical procedure.

The pH-base saturation relationship showed that the type of clay in the Astoria soil was similar to the 1:1 type and this appeared to be opposite from the results observed in the values of exchange capacities and the potentiometric titration curves.

All these factors lead one to suspect that the Astoria and Clatsop soils contain some amorphous substance which is responsible to a greater or lesser extent for their chemical behavior. This was observed by Birrell and Gradwell (2a, pp. 130-147). More information is needed to clarify this problem.

SUMMARY AND CONCLUSION

Five soils representative of the coast and the Willamette Valley have been studied for their general chemical characteristics. Exchange capacity and exchangeable cations were determined by the ammonium acetate and the BaCl_2 -triethanolamine buffer methods. Exchange capacity was also obtained from conductimetric titrations which were run on each soil before and after destroying the organic matter. Potentiometric titrations were run before and after leaching each soil with HCl. Lime requirement was determined by Woodruff's method and also obtained from the pH-lime curves.

The results indicate that the two coastal soils have lower pH and base saturation and higher organic matter content and exchange capacity than those from the valley. Good agreement on the results of the exchangeable bases as measured by different methods was obtained except for potassium for which no explanation can be given. The amounts of exchangeable aluminum determined by the procedure recommended by Peech are much higher in the coastal soils than those from the valley. More work should be done in order to substantiate how much of this amount of aluminum is exchangeable.

The determination of exchange capacity has been accomplished on both the original soil and the soils treated with hydrogen peroxide so that the portion of the exchange capacity attributed to the organic fraction could be estimated approximately. The results for the original soils showed that considerable higher

exchange capacities for the coastal soils than those for the valley soils were obtained. This difference might be due to the organic matter content. However, with similar amounts of organic matter in the valley soils, the Melbourne soil had higher exchange capacity than those for the Olympic and Willamette soils. This suggests that the type of clay mineral in the former might be different from the latter two. The results for the peroxide treated soils indicate that the organic fraction contributes about 65 per cent to the exchange capacity for the Olympic and Willamette soils but only about 50 per cent for the Melbourne, Clatsop and Astoria soils. This might further indicate that the type of clay mineral in the former two soils is different from that in the latter three. The values of the exchange capacities before and after the removal of organic matter were generally in agreement between the two different methods for the three valley soils but not for the coastal soils.

The buffering properties of the soils were studied by titrating the original soils and HCl-leached soils directly with 0.1N NaOH. The titration curves for the original soils indicate that the buffering characteristics of the coastal soils are quite similar, being well buffered through the whole pH range, while the valley soils are grouped together and slightly buffered, requiring less amount of base than the coastal soils for neutralization. When the soils were leached with HCl the shape of the curves for the Astoria, Clatsop, Olympic and Willamette soils were not changed except that the position of each of the curves was lowered with

increase in degree of base saturation since the exchangeable bases were replaced by hydrogen. In other words, these curves still maintain the same weak acid properties as those in the original soil. This indication might suggest the possibility that no exchangeable Al occupying the exchange spots had been replaced by hydrogen. In the Melbourne soil, however, the shape of the curve differs from that of the original soil, being buffered at low pH values and showing a strong acid property which suggests that some exchangeable Al had been replaced by hydrogen. The results from the titration curves appear to be in conflict with those obtained by the chemical procedure in that the exchangeable aluminum is much higher in the coastal soils than those of the valley soils. Therefore, the "exchangeable aluminum" as determined chemically was probably from some amorphous substance which might exist in the soils.

The pH values increased and the exchangeable acidity decreased with additions of lime in every soil studied. There was good agreement between the two methods in the determination of exchangeable calcium as long as the soils were unsaturated. When lime was added above the saturation point the amount of exchangeable calcium as determined by the ammonium acetate method increased but remained relatively constant for the barium chloride buffer method. The variations in exchangeable acidity and calcium between the two methods might be due to the following reasons:

1. Inability of NH_4OAC to replace the acidity especially

in the soils containing 1:1 type clay minerals and high organic matter content and resulting in the low values of the exchangeable acidity as well as the exchange capacity.

2. Ammonium acetate dissolves some free Ca-carbonate present in soils consequently a high amount of exchangeable calcium was brought into solution by the ammonium acetate solution.

The amount of lime required to bring the soils to a given per cent base saturation was quite different for different soils, depending upon the exchange capacity and the initial degree of base saturation. The coastal soils required 3 to 4 times as much lime as that needed for the valley soils. With similar exchange capacities but a lower degree of base saturation, the Astoria soil required more lime than did the Clatsop soil to obtain 100 per cent base saturation. The same thing was true in the case of the Olympic and Willamette soils. The Melbourne soil had both a higher exchange capacity and degree of base saturation than those of the Olympic and Willamette soils. Consequently, it needed less lime than the other two valley soils to obtain 100 per cent base saturation.

Theoretically, the sum of the exchangeable cations ought to be equal to the magnitude of the exchange capacity. The sums of the exchangeable cations determined for all the soils studied are relatively constant and close to the exchange capacity when measured by the BaCl_2 -buffer procedure. This might suggest the

reliability of the BaCl_2 -buffer methods for the determination of the exchangeable cations and the exchange capacity as compared to the ammonium acetate method where the exchangeable hydrogen is not a direct determination but is usually found by difference.

The relationship between pH and base saturation has been shown graphically. Different shapes of curves can be observed in different soils. The curves for the coastal soils are parallel and show a linear relationship between pH and base saturation. Inflection points occur at high degrees of base saturation and the slopes of the curves are steeper in the case of the barium chloride method. The curves for the valley soils are parallel only at the lower portions and then approach a common end point as the degree of base saturation increases. Inflection points occur at lower degrees of base saturation for the Olympic and Willamette soils but at a high degree of base saturation in the case of Melbourne soil. When the degrees of base saturation were compared at pH 7, there was some indication that the type of clay minerals in the Clatsop and Melbourne soils are similar to the 2:1 type while those in the Astoria, Olympic and Willamette soils are similar to the 1:1 type. This is contradictory with the results observed for the exchange capacity and potentiometric titration curves which indicate that the Astoria soil might contain 2:1 type as a predominating clay mineral. Whether some amorphous substance or organic matter in the Astoria soil would influence its pH and cation exchange properties requires further investigation.

It can be observed from the pH-base saturation curves that different degrees of base saturation are obtained at a given pH value for the different soils. Much more lime is required to bring the soils to a desired degree of base saturation when determined by the BaCl_2 -buffer method than by the ammonium acetate method. If the concept of base saturation as defined by Bradfield and Allison is used in the study of soils then the pH-base saturation relationship as determined by BaCl_2 -buffered method seems to be more reliable than that by the ammonium acetate method.

The determination of lime requirement was made both by Woodruff's method and the incubation procedure. Both methods indicate that much more lime is required to bring the coastal soils to a desired pH than the valley soils. Good agreement between the Woodruff method and the incubation procedure was obtained in the valley soils, but not in the coastal soils which appeared to need more than twice as much lime when determined by the latter method than was predicted by the Woodruff method. The evidence obtained from the exchange capacity, exchange acidity by the BaCl_2 -buffer method, buffer properties, pH-base saturation relationship and the base-saturation-lime relationship of the soils is fairly conclusive that the two coastal soils actually require as much lime as estimated by the incubation procedure to neutralize the soil acidity which might not be completely neutralized by the buffer solution recommended by Woodruff. It should be emphasized also, that from the standpoint of crop production, it is doubtful whether

17 or 18 tons of lime is actually necessary to obtain the maximum production for these soils. Thus, more laboratory, greenhouse, and field work is required to solve this question.

The results so far obtained suggest that the coastal soils might contain 2:1 type clay minerals, Olympic and Willamette soils might have 1:1 type as the predominating clay minerals, while those in the Melbourne soil appear more closely related to the coastal soils. However, some peculiar results occurred in the Astoria and Clatsop soils which might be due to the type of organic matter present or may indicate the presence of some amorphous substance. Further investigation concerning the chemical properties of both the inorganic and organic fractions in the coastal soils are needed.

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