SOME FACTORS AFFECTING ANION RETENTION IN ACID SOILS

by

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INTRODUCTION

Anion retention by soil was first discussed by Mattson in 1927. Since his work, only a small amount of interest has been shown in this field until recently. Most of the investigations have been concerned with the retention of phosphate. Some properties of soils related to anion retention have been shown experimentally. Soils with high iron content, and high clay content but low organic matter content and low cation exchange capacity exhibit higher anion retention. Anion retention has been found to increase with decreasing pH, and to increase with increasing anion concentration. Anions such as phosphate and sulfate are more strongly held by soils than are chloride and nitrate. Hence, the latter can be replaced by the former.

Some workers have suggested that the mechanism of anion retention is the same as that of cation adsorption on clay, owing to the amphoteric properties of clay. Others have reported the simultaneous adsorption of both cation and anion, and referred to this as molecular or salt adsorption or electrolyte inbibition. Still another suggestion is that anions exchange with the hydroxyl groups dissociated from the aluminum or iron hydroxides of the soil.

The importance of an understanding of anion retention is evident because of its consequences: (1) anion retention will result a decrease of available soil nutrients and leaching of the applied nutrients, thus affecting the uptake of soil nutrients by plant roots and other related problems in soil fertility. (2) It confuses the measurement of cation exchange capacity by the methods now used by most soil scientists, and makes the cation exchange capacity an uncertain quantity. (3) Changes due to the adsorption and desorption of anions may cause changes of soil physical properties which directly or indirectly influence plant growth.

The objectives of this study were: (1) To use chromatographic methods to study the effect of pH and the effect of anions themselves on the anion retention in an acid, red soil. (2) To investigate the effect of time of equilibration on anion retention by soil. (3) To arrive at a mechanism for anion retention which would explain all the known facts of the phenomenon.

LITERATURE REVIEW

I. Effects of pH and Solute Concentrations on Anion Retention:

In 1927 and 1931, Mattson first reported studies on anion adsorption by soil colloidal materials of varying $SiO_2/Al_2O_3 + Fe_2O_3$ ratio. He found that in acid solution Cl^-, $SO_4^=$ and $H_2PO_4^-$ were adsorbed, whereas only phosphate ion was adsorbed from alkaline solution. The quantities adsorbed decreased with a decrease in hydrogen concentration, which was ascribed to a displacement of anions by the hydroxyl ions. When acid was added to the soil solution the effect was to reduce the net negative charge of the soil material. Thus, Mattson pictured soil materials as possessing amphoteric properties, combining with anions as well as with cations; the relative amounts of each depending upon the pH. Earlier than this, Miller (1924) found a marked decrease in sulfate adsorption by aluminum hydroxide at pH values greater than 5.5. He attributed this to the stronger coordination of the hydroxyl than the sulfate ion with aluminum. As the OH^- concentration increased, it replaced the sulfate from the basic aluminum sulfate precipitate. Kamprath et al. (1956) obtained the same sort of results while working on the adsorption of sulfate by soils; i.e., the amount of sulfate adsorbed decreased as the pH of the soil suspension increased from 4 to 6. Ayres (1941) found while studying the sorption of potassium and ammonium by Hawaiian soils, that a lowering of pH imparted a marked increase to the capacity of soils to retain sulfate.

Davis (1935) showed the degree of sorption of phosphate by Hawaiian soils is a function of the hydroxyl ion concentration of the solution. In accordance with the Donnan Equilibrium, he developed a theoretical basis for this fact. Murphy (1939) observed that "ballmilled" kaolin was very effective in sorbing phosphate from solutions containing $H_2PO_4^-$ ions and that sorption increased to a maximum progressively as the pH of the solution was decreased to pH 3.0. At pH values below 3.0, decomposition of the mineral prevented further fixation. This was proved by measuring the water formed by the interaction of phosphate with ballmilled kaolin and halloysite, and from x-ray data obtained from the phosphated minerals. Sieling (1946) also found the sorption of both phosphate and arsenate ions increased markedly with increasing acidity of the solution from pH 7.0 to pH 3.3. This was in agreement with the previous work of Toth (1937) on adsorption of phosphate by soil colloids. Black (1942) concluded that the fixation of phosphate by replacement of the hydroxyl groups of kaolinite is dependent upon a number of factors which included the degree of subdivision of clay, the pH of the solution, the concentration of phosphate ions, and time of contact.

Schofield (1939, 1946) found that the magnitude and sometimes even the sign of the charge the clay carries depend upon the pH. Almost all the clays studied carried a negative charge at the neutral point. The negative charge increased if the clay was made alkaline. These observations support Mattson's observations (1931).

Recently, Berg and Thomas (1959) worked with soil columns, adding salts from the top and eluting with water. They calculated the amount of anions held in the soil column. Their results showed that under moderately acid conditions (pH4 to pH6) chloride was not retained in soils against water washing, whereas sulfate was retained. Berg (1960) concluded that the anions adsorbed by the Fe-kaolinite-complex from salt solution depended upon the anion, equilibrium concentration, pH, and amount of iron present. Sieling (1946) showed in his work on phosphate and arsenate adsorption by kaolin, that the amount of either anion sorbed was dependent upon the reaction (pH) of the equilibrium solution and the initial concentration of the solution. Rovikovitch (1934) explained that a weak concentration of solution gave less adsorption of phosphoric acid than the exchange capacity of H-soil because the exchange between phosphoric acid ions and the anions of the soil complex was incomplete. As the concentration of phosphoric acid ion was increased, the anion exchange became complete. He observed the same adsorption in Ca-soil. Kurtz et al., (1946) plotted the amount of phosphate adsorbed by the soils on a logarithmic scale against the logarithm of the concentration of phosphate remaining in solution and a straight line was obtained for a considerable range of concentration for all three different soil-solution ratios. Kamprath et al. (1956) found the same correlation between the concentration of sulfate in solution, and the amount of sulfate adsorbed by soils. They also showed that the adsorption of sulfate by the Cecil soil at pH 4 and 5 approached a maximum at a concentration of 400 ppm of sulfur in solution under the conditions studied. Kunin (1958) studied the titration with acid of amberlite IR4B resin, and found an increase in adsorption at any fixed pH with increasing salt concentration when both dilute (0.01N HCl) and concentrated (1.0N HCl) acid were used for titration. Similar results were obtained for the titration with HNO_3 and H_2SO_4 in solutions of KNO_3 and K_2SO_4.

II. Anion Effects

Mattson (1927, 1930, 1931) found that the adsorption of anions by soil colloidal material increased in the order $Cl^- < SO_4^= < SiO_3^= < H_2PO_4^- < OH^-$. In 1923, Lichtenwalner had found the same results with aluminum and iron gels. He found that NO_3^- underwent only slight adsorption. The order was $NO_3^- < SO_4^= < H_2PO_4^-$ and the absorbed nitrates were quickly washed out by H_2O. The sulfate was washed out less quickly, while the phosphate was held very persistently. Further, sulfate ions were shown to be completely replaced by phosphate ions in both gels. Kamprath et al. (1956) found that an increased concentration of phosphate in the solution reduced the amount of sulfate adsorbed by soils. Only slightly more phosphate than sulfate was adsorbed by Cecil soil when each was shaken separately with the soil in nearly equivalent concentrations, however. It was suggested that in Cecil soil, sulfate and phosphate were adsorbed by the same mechanism. They showed that sulfate adsorption was completely stopped in all the soils studied by the presence of only 2/3 of the equivalent amount of phosphate compared to sulfate. This is in agreement with the previous work of Lichtenwalner (1923). Ensminger (1954) reported that in field studies increasing amounts of superphosphate applied to a Cecil clay loam resulted in decreasing amounts of sulfate being retained. This suggested that phosphate and sulfate apparently compete for the same sites.

Ayres (1941), and Ayres and Hagihara (1953) studied the adsorption of potassium by some humic and hydrol humic latosols in Hawaii, and found the ability of the soils to retain potassium from KCl is very slight, from K_2SO_4, considerable, and from various phosphates of potassium, marked. Substantial percolation losses of potassium from these three salts started and ended in a successive series; i.e., losses from KCl occurred before there was any from K_2SO_4, etc. Kunin (1958) using the hydroxyl form of Amberlite IR4B resin to obtain acid titration curves, found the order of increasing adsorption at any fixed pH was $HCl < HNO_3 < H_2SO_4 < H_3PO_4$. The order of regenerative power was $NaOH > Na_2CO_3 > NH_4OH$.

The regeneration of sulfate salt of the resin was more difficult to accomplish than that of chloride salt. The extent of regeneration apparently depended upon the pH of the regenerant. Schofield and Samson (1953) showed that Cl^- and NO_3^- were held rather weakly by kaolinite. Recent work of Berg and Thomas (1959) also concluded that $SO_4^=$ was held much more tightly than was Cl^-. Later Thomas (1960) used a chromatography technique to study the effect of "electrolyte imbibition" by soils on their cation exchange behavior, and calculated anion distribution coefficients (K_d). He found that these coefficients varied in the order $Cl^- = NO_3^- < SO_4^= < H_2PO_4^-$ on a kaolinitic Ca-Lloyd soil whereas only $H_2PO_4^-$ had a K_d above zero on the montmorillonitic Yolo soil.

III. Mineralogical Effects

In 1956, Kamprath et al., studied some of the factors affecting sulfate adsorption using Cecil, White Store and Nipe soils and a H-Al bentonite. They found that soils which contained relatively large amounts of two-layer type clay minerals adsorbed more sulfate than did soils containing predominantly three-layer clay minerals. Berg and Thomas (1959) concluded that anion adsorption occurred in soils which were high in kaolin clays and aluminum and iron oxides. A soil dominated by 3-layer clays showed little or no attraction for Cl^- or $SO_4^=$. Early in Mattson's work (1927, 1930), anion adsorption was related to oxides of iron and aluminum in soil colloidal materials as compared SiO_2 content. Since kaolinite has a lower SiO_2: Al_2O_3 ratio than does montmorillonite, the observations assisted by X-ray diffraction agree with those done by total chemical analysis.

Mattson (1927) and Toth (1937) concluded that the adsorption of anions from solution is probably chiefly due to the iron oxide. Joffe and McLean (1927), on the other hand, found that sulfate and phosphate anions suppressed the solubility of Aluminum. Ensminger (1954) reported that dehydrated Al_2O_3 adsorbed much more sulfate than any of the other materials studied. The iron minerals used adsorbed small amounts while the Davidson colloid, kaolinite and bauxite were intermediate. Lichtenwalner (1923) showed that aluminum oxides adsorbed more sulfate than did iron oxides. Coleman (1945) reported that kaolinite and montmorillonite were able to fix only a small portion of the phosphate which was fixed before the free iron- and aluminum-oxides were removed. This indicated that the free iron and aluminum, but not the clay minerals, were largely responsible for the fixation of phosphate. Toth (1937) found that the same thing happened in Cecil colloid (12.3% free iron oxides). He reported that removal of the free iron oxides caused a reduction of the adsorption of P_2O_5 from 0.370 to 0.25 me/gm. The reduction in a similarly-treated Sassafras was from 0.275 to 0.125 me/gm. He also found that the adsorption of silicates and phosphates by the Colts Neck and Cecil colloids reduced the free iron oxide content. The freeing of exchange sites in the two colloids was verified by determining the exchange capacity of these colloids before and after the removal of the free iron oxides. Black (1942) concluded that in Cecil clay the action of iron and aluminum was an important factor during the fixation at pH 5 to pH 7. Heck (1934) reported that in later tests, large quantities of the hydrated oxides of iron and aluminum are present and due to their presence, the effect of the ratio of active calcium to active iron and aluminum on adsorption of phosphate was overshadowed. Mehlich (1952) found that soils high in kaolinite, iron oxide and gibbsite show a high affinity for anions, which is in agreement with other investigators. Schofield (1939, 1946) observed the finer the material the greater the hydroxyl groups calculated from the increase of charge on the alkaline side of the neutral point. Lin (1959) obtained the same result as Mattson (1927) on adsorption of Cl^- and $SO_4^=$ by Davidson and Cecil soils.

Recently, Franklin and Reisenauer (1960) working on Northwestern soils, reported that there was no evidence of any relationships between the anion-exchange capacity (AE C) and total clay, kaolinite, or three-layer mineral content of these soils. Low values for AEC were obtained on soils with either highest and lowest contents of clay, kaolinite and three-layer minerals. High AE C values were found on soils of very low kaolin content but with at least 25% clay. Very high values for AEC were found only on the fine textured soils. The existence of a relationship between phosphate sorption and clay content would imply that the properties of the soils, other than texture were similar. Type or content of clay are only indirectly related to the capacity of these soils to sorb phosphate. Therefore, he concluded that phosphate sorption was highly correlated with the exchangeable Al and citric-acid solution Al contents of the soils, but not related to either the type or content of clay.

IV. Time Effect

Lichtenwalner (1923) worked with colloidal oxides of Fe and Al and reported that the time required for equilibrium was a function of the amount of shaking and the rate of adsorption. Sieling (1946) found that a value approaching maximum absorption of phosphate and arsenate by ball-milled kaolin was not reached until the time exceeded 144 hours.

Rovikovitch (1934) studied the anion exchange reaction for Ca-soil and found that during the first few minutes of contact between the soil and solution, 90 percent of the hydroxyls which take part in the exchange reaction are replaced by the monovalent ($H_2PO_4^-$) phosphoric anions in H-soils. The exchange reaction with the trivalent ($PO_4^{\equiv}$) phosphoric anions proceeds much more slowly. Coleman (1945) in his studies of phosphate fixation with kaolinitic and montmorillonitic fine clays found that within the pH range of most soils (pH 5 to 7), the clays fixed almost as much phosphate in 24 hours as in 1 month, but in the more acid reaction (below pH 5) both clays fixed considerably more phosphate in one month than in 24 hours. He suggested that there were two different mechanisms for fixing phosphate. One operated above pH 5 which fixed phosphate immediately, and the other below pH 5 and fixed phosphate more slowly.

Kurtz et al., (1946) studied the effect of time on phosphate adsorption. His data showed that the reaction was not complete after any particular time interval (up to 70 days) in Illinois soils. Black (1942) also mentioned that the time of contact is a factor of adsorption.

V. Mechanisms:

Soil material possesses amphoteric properties, combining with both anions and cations depending upon pH. Mattson (1927, 1930) first introduced this concept to account for anion adsorption. Following his ideas, many investigators postulated that there were positive as well as negative charges on clay minerals. Some (c.f., Ayres and Hagihara, 1953) concluded that the adsorption of anions and cations was simultaneous and perhaps molecular. Kurtz et al. (1946) concluded that since the colloidal particles are made up of both positive and negative layers, the over-all negative charges did not preclude the existence of local areas of positive charge where adsorption of negative ions could take place

(Schofield, 1939). Later Schofield (1949) suggested that positive charges might be created by the transfer of protons from H_3^+O to an oxygen of the hydrous ferric oxides. An oxygen capable of adsorbing an additional proton might occur at the edge of the regular crystal or as a result of imperfect crystallization. Schofield and Samson (1953) explained that the flocculation phenomenon of kaolinite was a result of the electric attraction between the positively charged edges and negatively charged faces of the adjacent platelets.

Recently, Berg (1960) stated a theory as an explanation for the adsorption phenomena. Summing up all the mechanisms suggested by the earlier investigators, he suggested that the positive charge on the iron oxide may be due to dissociation of hydroxyl groups.

Chao (1960) worked with soil columns to study the movement and adsorption of sulfate ions in soil. He ascribed anion retention to the positive charge developed on hydrous aluminum or iron oxides, or on the crystal edge of kaolinite clays at low pH values. He also suggested that soil organic matter may develop positive charges under certain specific conditions. This seems to be a conclusion of most workers. Even before Mattson, however, another idea was published by Lichtenwalner (1923). He found that the ions of salts were taken up by iron hydrogel in nearly equivalent quantities. He postulated that there was an adsorption of molecules as a whole. Davis (1935) also found that cations are adsorbed along with the phosphate at various pH values in a ratio of 3 equivalents of cations to 1 mol. of phosphorus held. In 1934, Thomas mentioned two explanations as possibilities: preferential adsorption of Fe^{+++} or H^+ ions. He presented the situation as

$$Fe_2O_3 \cdot H^+ Cl^- \quad \text{or} \quad Fe_2O_3 \cdot Fe^{+++}\ 3\ Cl^-$$

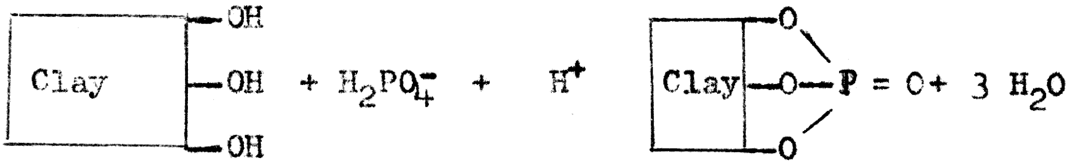
(ignoring water of hydration). Thus the anions were adsorbed along with the cations. Ayres and Hagihara (1953) also found in humic and hydrol humic latosols that retention of potassium from K_2SO_4 and K_3PO_4 proceeded without recovery of measurable quantities of displaced cations in the leachates. This strongly suggested that the anion might have been sorbed along with the potassium. They also found that phosphate was not leached from the K_3PO_4 - treated soils, nor under moderate leaching was sulfate lost from soils that received K_2SO_4. He interpreted these results as implying a simultaneous sorption of both the cation and the anion of these salts. Chao also showed evidence of the simultaneous adsorption of sulfate ion with the associated potassium ion, concluding that this salt adsorption "resulted from attraction due to physical force between electrolyte molecules and the surface of the soil colloid." Berg (1960) showed that simultaneous adsorption of cations and anions occurs in Fe-cellulose powder complex. Ensminger (1954) found that phosphate released sulfate and decreased the capacity of soils to adsorb sulfate and came to the conclusion that sulfate and phosphate were adsorbed by the same mechanism. Overstreet and Dean (1951) postulated that the mechanisms by which chloride, sulfate, and phosphate ions were retained in a Cecil soil were similar.

Rovikovitch (1934) suggested that the equivalent exchange reaction which was characteristic of cation exchange existed also for anions. The exchange reaction, which began as $Ca(OH)_2$ and NaOH solution were added to the soil, proceeded in two phases. In the first phase, only a cationic exchange took place, between the calcium or sodium ions of the introduced solution and the exchange hydrogen ions which are in equilibrium with the hydroxyl ions. As the replacement of the hydrogen ions was completed, the second phase proceeded. This exchange was anionic as well as cationic. It proceeded between the calcium or sodium ions of the solution and the exchangeable hydrogen ions which are in equilibrium with the adsorbed phosphate ions. About the same exchange reaction was observed by Kelly and Midgley (1943) and McAuliffe et al. (1947). They concluded that phosphate fixation was a physicochemical exchange of phosphate ions for exposed hydroxyl ions. Kaolin retained phosphate only when it was finely ground to expose active hydroxyl ions. When a suspension of any material studied was mixed with soluble phosphate of similar pH, the resultant mixture increased in pH which indicated the replacement of hydroxyl ions by the phosphate ions. Furthermore, dehydration and removal of hydroxyl ions by high temperature greatly reduced the phosphate fixation capacity and hydrated iron oxide.

Early in 1939, Schofield also theorized that soils might develop negative or positive charge by acid dissociation or basic dissociation respectively. Berg (1960) further postulated that anion adsorption from salt solution by iron oxide-clay systems might occur at either those positive sites on the iron oxide that had not interacted with clay, or those that had interacted with the clay. If it was in the latter case, a negative site on the clay becomes available for cation adsorption. This may be what was happening in Rovikovitch's second phase. It appears that anions exchange with hydroxyl ion, becoming a part of the iron- or aluminum-hydroxyl system. The idea that anions are adsorbed at positively charged sites is actually the same as the anion being adsorbed by exchange with hydroxyl ions.

Black (1941, 1942) found that a longer period of contact was needed for the slow penetration of phosphate between the lattic layers and replacement of hydroxyl ions not directly exposed to the solution. A large proportion of the phosphate fixed by Cecil clay, presumed to be held by OH replacement, could be washed out with water, but this was not true in kaolinitic clay (1 ppm phosphorus solution). The phosphate held by the ferric iron oxide component was removed more slowly. The last mentioned kind of fixation may be due to the formation of an insoluble compound. Recent work by Kittrick and Jackson (1959, 1960) showed that phosphate reacted with the mineral greenalite(an iron kaolin) and kaolinite at room temperature to form new separate phases, apparently of strengite and variscite, respectively.

Coleman (1945) suggested that phosphate replaced hydroxyl ion from the free iron and aluminum hydroxides rather than from the clay minerals alone. Stout (1940) pointed out that the relative abilities of kaolinite and bentonite to fix phosphate were related to the hydroxyl ions available for exchange with phosphate ions. According to him, this availability may depend upon pH, which controls the dissociation of hydroxyl groups. The phenomenon of phosphate fixation by ground kaolinite and halloysite was a reversible ionic exchange between phosphate and hydroxyl of the crystal lattice. The loss of H_2O from the kaolinite is of an order of magnitude requiring the inclusion of hydroxyl ions from the crystal lattice. The reaction is:



Thus the products of the reaction were phosphated kaolinite and water. This is in agreement with the conclusion of Kelly and Midgley (1943).

Low and Black (1950) explained that the rate of release of silica during phosphate fixation by kaolinite varied with time, indicating the existence of two different reactions. The first and more rapid reaction was complete before the second began. They believed the first one to be the surface replacement of silica tetrahedra by phosphorus tetrahedra, and the second to be phosphate-induced decomposition of the clay to form an aluminum phosphate compound. In dilute solution, only the first reaction occurred. Silica entry into solution also can be explained by decomposition of clay, and the formation of aluminum phosphate, however. In some resin work done by Kunin (1958) he reported that strong base exchange resins were quite similar in their exchange reactions to the strong acid exchange resins and the reaction can be described as below:

$$R_4\,N^+\;OH^- + Na^+ + Cl^- \rightleftharpoons R_4N^+\;Cl^- + Na^+ + OH^-$$

$$R_4\,N^+\;OH^- + H^+ + Cl^- \leftrightharpoons R_4N^+\;Cl^- + H_2O$$

Where acid is added to the system the hydroxyl ion may be replaced by the anion of the acid, and the H^+ ion neutralized by the hydroxyl ion. Jenny (1946) also indicated the exchange of anions for hydroxyl groups in exchange resin. Bishop (1946) believed anion adsorption on resin was due to the formation of covalent bonds between the nitrogen of the resin and the hydrated proton of the acid whereas the anion was retained by electrostatic attraction. Kunin and Myers (1947) explained that the idea of an adsorption of whole molecules was based upon the fact that in neutral and basic solution no adsorption of anion was evident. In acid solution the OH^- activity was weak enough to allow dissociation of the base and for anion exchange to occur. The resin used was weakly basic, but the pH of the equilibrium solution formed on the addition of a neutral salt to the hydroxyl form of the resin was alkaline and the alkalinity was increased with the increasing concentration. This was taken as proof of the existence of OH groups.

MATERIALS AND METHODS

I. Equilibration of Sulfate and Chloride in Soils.

Soil columns were made with ten gm. of Cecil clay ($<2\mu$ Cecil B_2 horizon taken from near Dixie, Virginia, on U.S. Rt. 15) which was well mixed with an equal weight of ashless, Whatman Cellulose powder. Above and below this mixture were placed small quantities of cellulose powder. These were added to prevent the clay particles from running through the bottom of the column and to stop the formation of channels in the soil column when solution was dropped from the top. Solutions were made up with 0.01N K_2SO_4 and 0.01 N KCl solutions mixed in various ratios and "spiked" with S^{35} (30μC/liter).

The entire column (including glass column, soil and cellulose powder) was weighed dry. The column then was set up and solution was added to the top of the column, drop by drop at a rate of approximately one ml. per minute. A 250 ml. separatory funnel containing the input solution was attached to the column by a rubber tube and a short glass tube going through a one hole rubber stopper. When equilibrium was attained, i.e., when the radioactivity of S^{35} in the effluent appeared to be equal to that in the input solution, the solution in the column was replaced with tracer-free 0.01N K_2SO_4 until essentially zero radioactivity was obtained in the effluent. The effluent was collected in a flask, and made up to volume.

The radioactivity of both the original solution with known sulfate concentration and the effluent were sampled by 1 ml. aliquots from both solutions, placing each of them on an aluminum planchet, and drying. Measurement of the sulfate activity was carried out with a Nuclear Chicago Geiger-Müller counter tube, model D-47, and scaler, model 183 B. Measurements were taken at 1300 Kv. and 5 lb. pressure of Q-gas. Before the sample measurements the counter and scaler were checked with a standard made with C^{14} to assure that it was warmed up. The background also was checked. Chloride contents of the input and effluent solutions were determined by potentiometric titration, using a Beckman Model G pH meter and a silver-silver chloride electrode.

The wet weight of the entire column was taken and the amount of solution held was calculated. The amount of Cl and SO_4 actually held on the soil then was obtained by the relationships.

Cl adsorbed = Cl titrated - (Wet Wt. - Dry Wt.) (<u>N</u> of Cl in input solution)

SO_4 adsorbed = (SO_4 activity) (ml effluent) - (Wet Wt.- Dry Wt) (Activity of input solution)

II. <u>Time Effect</u>

In general, samples were weighed out and put in polyethylene bottles. To each sample was added solutions (as described in the following for each different case). The bottles were put on a shaker and shaken for various time periods. At the end of each time period, the bottles to be analyzed were centrifuged to obtain a clear supernatant, which was analyzed in various ways.

Cecil clay ($<2\mu$), Cecil soil (<60 mesh) and iron-treated Georgia kaolinite (a,b) were used as anion adsorbing materials. Analyses were carried out in three different ways.

(1) Two gm. of Cecil clay or 5 gm. of Cecil soil were used. Fifty ml. of $0.01\underline{N}$ K_2SO_4 "spiked" with $35\mu C$ of S^{35} per liter was added to each soil or clay. The sulfate left in solution after each time period was determined by radioactivity measurement as in Section I and the amounts of sulfate held in soil were obtained by subtracting the sulfate left in solution from the total amount added.

(2) Using duplicate five gm. samples of Cecil soil, $0.01\underline{N}$ K_2SO_4 or $0.01\underline{N}$ KCl were added to bottles. Volumes of solution used were 50 and 100 ml.

Time periods from one minute up to four weeks were studied. The cations Ca^+, Mg^{++}, and K^+ in the supernatant were determined by flame photometric methods, and Al^{+3} was estimated by the colorimetric method of Jones and Thurman (1957).

(3) To 1000 gm. Ga-kaolinite, two (51.93 and 81.47 m. mol. Fe/100 gm.) different amounts of iron were added by gentle heating with $\underline{N}$ $FeCl_3$, followed by water washing. Iron contents were determined by Jackson's procedure (1958). From

these two Fe-kaolinites, 15 gm duplicate samples were taken. Fifty ml. of 0.02N K_2SO_4 was used.

The conductivity of each supernatant liquid was measured using a Model RC-16 B Conductivity Bridge at 60 cps. pH of each supernatant was determined using a Beckman zeromatic pH meter.

III. <u>Distribution Coefficient Determinations</u>

Twenty gm. of Cecil soil was mixed with an equal weight of cellulose powder, and the soil column prepared as in I. The dry weight of the entire column was taken and the column was set up on the fraction collector. Column pH was adjusted by adding either mixtures of salt and acid in different ratios or mixtures of base and salt, then, washed with various volumes of distilled water. To obtain the "Pore" volume of the column, it was weighed wet and the difference between the dry and wet weights were taken as the amount of water needed to saturate the column.

Solutions used for the experiment were 0.2N NaCl, 0.2N KNO_3 and 0.2N K_2SO_4, "spiked" with S^{35}. Two and one-half ml. of each solution was added from the top of the wet soil column and bled in. Following this, distilled water was run through the column at a rate of about one ml. per minute until the effluent contained essentially no anions. Five ml. fractions were collected in test tubes using a Model 1205 - D - 3 Reco automatic fraction collector. Chloride ion content was determined by the potentiometric method given in I. Nitrate was determined by the procedure of Jackson (1958). One-tenth ml. aliquots of $SO_4^=$ effluent were taken from each 5 ml. fraction and the activity compared with that of a standard. Counting methods used in section I were used.

The pH of the soil from each column was measured by removing the mixture and adding an equal weight of distilled water. A Beckman Zeromatic pH meter was used. Distribution coefficients were calculated by the equation (Ketelle and Boyd, 1947):

$$Kd = \frac{(V - 1)\,E}{\rho}$$

Where, Kd = (Distribution Coefficient) =

$$= \frac{\text{me/100 gm. anion on soil}}{\text{me/100 ml. anion in solution}}$$

$$E \text{ (fraction of void space)} = \frac{\text{Volume of } H_2O \text{ held in column}}{\text{Volume taken up by soil and cellulose}}$$

ρ = (density of soil column)

$$= \frac{\text{weight of soil}}{\text{Volume taken up by soil and cellulose}}$$

V = (Volume of Solution needed to displace one-half of the anions)

$$= \frac{\text{Volume where peak appears}}{\text{Average column volume}}$$

RESULTS AND DISCUSSION

I. Sulfate-chloride Equilibrium in Cecil clay

The retention of chloride and sulfate by Cecil clay was achieved by eluting the mixtures of 0.01N KCl and K_2SO_4 until apparent equilibrium was reached. Results are shown in Table 1. Chloride was held appreciably only when it made up 90 percent of the anion mixture. At ratios of C^{SO_4}/C^o, greater than 0.2, the amount of Cl held was small and nearly constant. The plot of C^{SO_4}/C^o vs q^{SO_4}/q^o is given in Figure 1. A value of $q^{SO_4}/q^o = 0$ when $C^{SO_4}/C^o = 0$, and, a value of q^{SO_4}/q^o of one corresponding to a C^{SO_4}/C^o ratio of one are assumed. The curve indicates that SO_4 was held much more tightly than was Cl. Identical affinities of Cecil clay for SO_4 and Cl would have caused the experimental points to fall on the dotted line.

The point at the C^{SO_4}/C^o ratio of 0.7 lies off the curve indicating a lesser amount of retained SO_4 than would be expected. Apparently, this resulted because the equilibrium was not reached. Examination of the sum of anions held (Table 1) reveals that it generally increased as the SO_4 in solution was decreased. During the experiments, it was found that "apparent equilibrium" took longer to achieve when the C^{SO_4}/C^o ratio was lower. For example, 70 percent SO_4 solution was run through the column for only a few hours,

Table 1

The equilibrium between sulfate (0.01N K_2SO_4) and Chloride (0.01N KCl) in Cecil clay

c^{SO_4}/c^o	q^{SO_4} me/100 gm.	q^{Cl} me/100 gm.	$q^{SO_4}+q^{Cl}$ me/100 gm.	q^{SO_4}/q^o
0.7	2.24	0.37	2.61	0.86
0.4	3.20	0.22	3.42	0.94
0.3	4.02	0.29	4.31	0.94
0.2	3.61	0.36	3.98	0.91
0.1	2.76	1.62	4.38	0.63

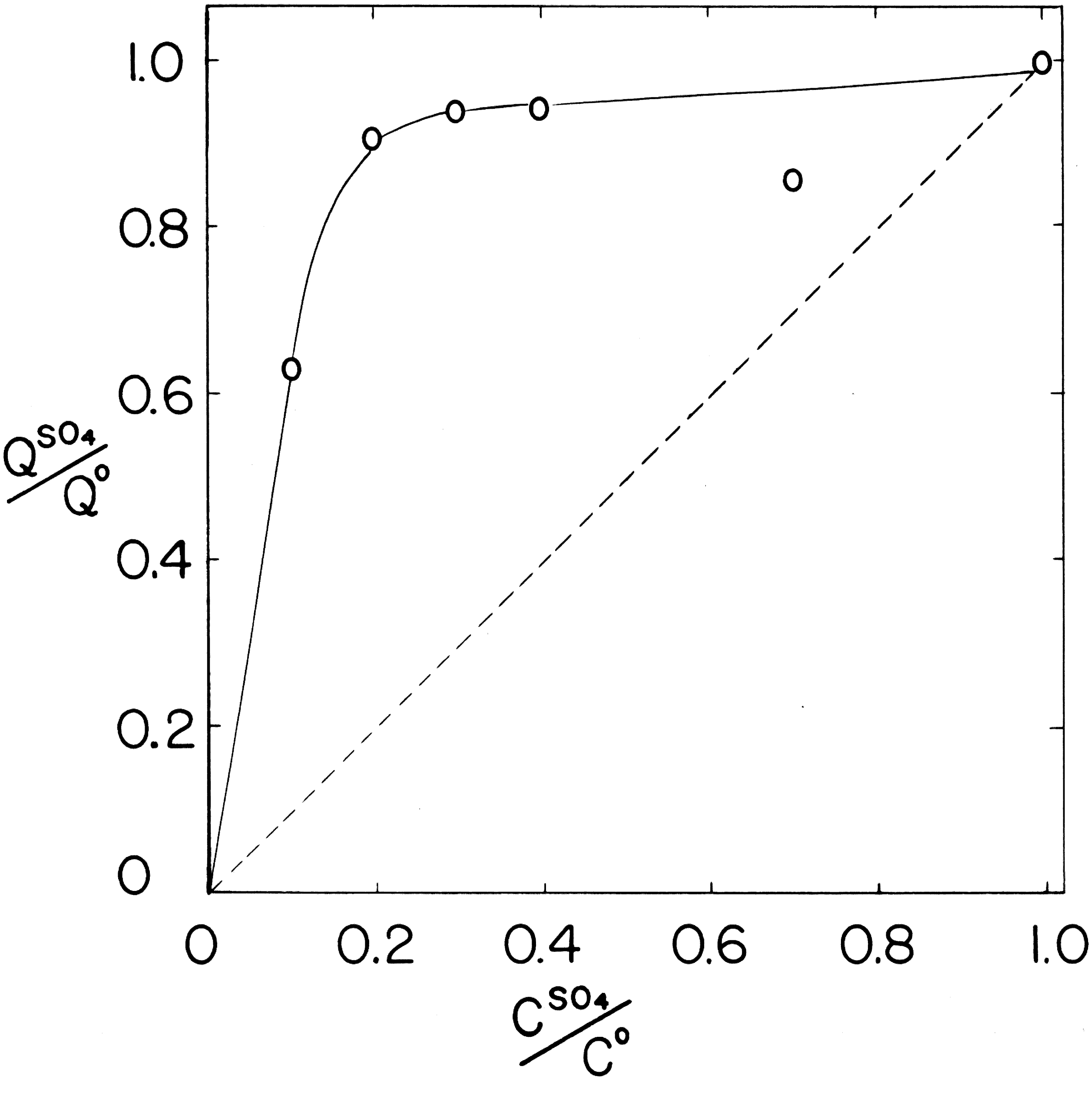


Figure 1. The effect of solute concentrations on the simultaneous adsorption of sulfate and chloride in Dixie Cecil clay.

whereas the 10 percent sulfate solution required about a week. Thus it appears that true equilibrium was not reached in the time studied, and that the sum of SO_4 and Cl retained was dependent on the time of equilibrium. These results led to a further study of the effect of time on SO_4 and Cl retained.

II. Time Effect on Anion Retention

The relation between anion adsorption and time of contact of soil and solution was further investigated in three ways. Table 2 shows the effect of time on the amount of sulfate adsorbed by Cecil clay and Cecil soil, which were shaken with 0.01N K_2SO_4 solution containing tracer amounts of S^{35}. As the time increased from one minute to 66 hours, SO_4 adsorbed increased from 2.25 to 2.90 me/100g. of clay and 1.30 to 2.10 me/100 gm. of soil. When the time was increased to four weeks in the case of Cecil soil, the adsorption of sulfate was increased to approximately 4.0 me/100 g. of soil.

From Figure 2, it is evident that the adsorption of sulfate ions by Cecil clay proceeds very rapidly at first, followed by a slow linear increase of sulfate retained with time. The reaction apparently is not complete even after four weeks according to data obtained with the Cecil soil. This agrees with results of Sieling (1946), Coleman (1945) and Kurtz et al. (1946) in their phosphate adsorption work.

Figure 4 shows the decreasing conductivity in 0.02N K_2SO_4 after equilibration with Fe-treated Georgia kaolinite from

Table 2

Time effect on the retention of sulfate by Cecil clay and Cecil soil

Equili. Time	Sulfate retained, me/100 gm.	
	Cecil clay	Cecil soil
1 min.	2.25	1.30
30 min.	2.35	1.41
1 hr.	2.50	1.50
24 hrs.	2.60	2.20
66 hrs.	2.90	2.10
1 wk.	---	2.40
2 wks.	---	3.24
4 wks.	---	3.60

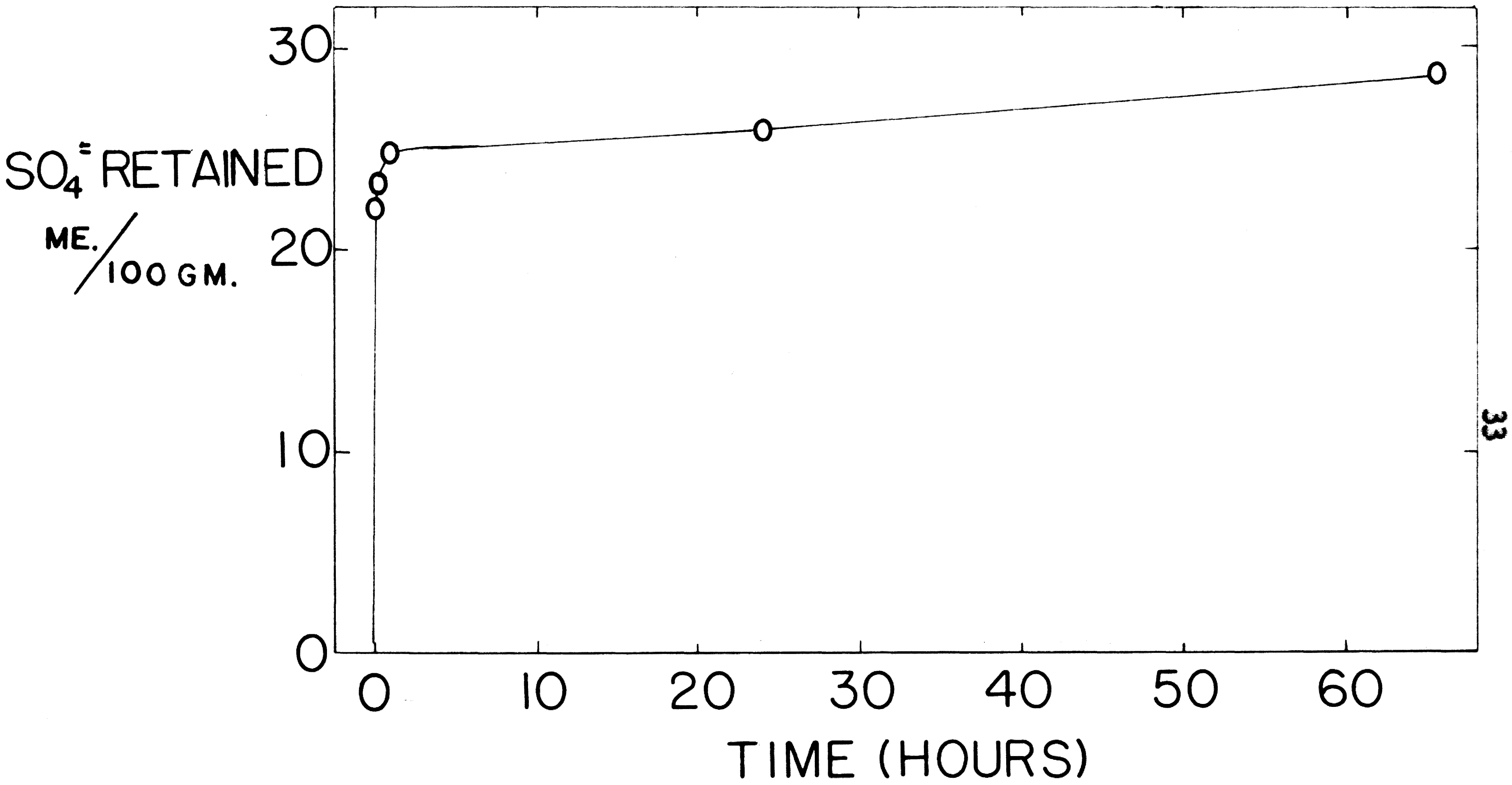


Figure 2. Effect of time on the adsorption of sulfate from 0.01N K_2SO_4 by Cecil clay.

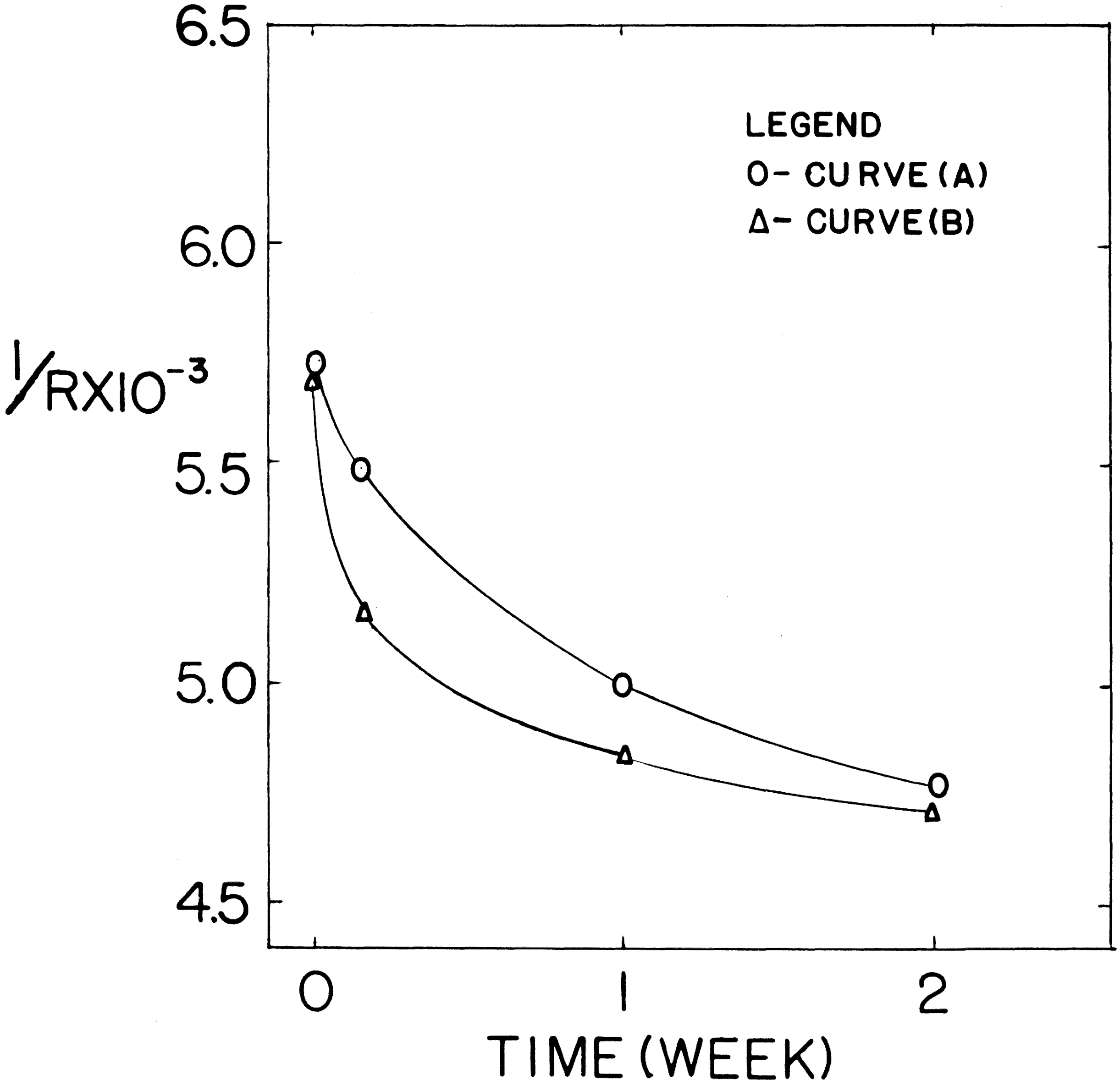


Figure 3. Effect of time on retention of salt as measured by conductivity in 0.02$\underline{N}$ K_2SO_4 solution in kaolinite with two different Fe-contents. (a) 51.93 m.mol./100gm. (b) 81.47 m.mol./100 gm.

Table 3 **Time effect on the amount of anions retained from 0.01N K_2SO_4 or 0.01N KCl solution by Cecil soil as measured by summing up the total cation disappeared from the solution.**

Solution added	Time	K	Ca	Mg	Al	EM$^+$ me/100 ml.	me/100 gm. Soil
100 ml.	1 hr.	0.845	.011	.045	.078	.979	0.42
0.01 N	24 hrs.	.815	.012	.040	.046	.913	1.74
K_2SO_4	1 wk.	.790	.011	.045	.052	.898	2.04
	2 wks.	.800	.011	.045	.048	.904	1.92
	4 "	.785	.013	.052	.049	.899	2.02
	8 "	.790	.011	.045	.036	.882	2.36
50 ml.	1 hr.	.350	.007	.032	.031	0.420	1.61
0.01 N	24 hrs.	.350	.009	.033	.020	0.412	1.77
K_2SO_4	1 wk.	.370	.009	.032	.029	0.440	1.20
	2 wks.	--	--	--	--	--	--
	4 wks.	.330	.009	.032	.022	0.393	2.14
	8 "	.330	.008	.032	.014	0.384	2.32

Table 3 (continued)

Solution added	Time	K	Ca	Mg	Al	EM^+ me/100ml.	me/100 gm. Soil
100 ml. 0.01N KCl	1 hr.	.985	.014	.057	.053	1.111	-2.22
	24 hrs.	.890	.016	.060	.053	1.019	-0.38
	1 wk.	.880	.014	.057	.052	1.003	-0.06
	2 wks.	.805	.020	.060	.055	0.940	1.20
	4 "	--	--	--	--	--	--
	8 "	.870	.014	.062	.072	1.018	-0.36
50 ml. 0.01N KCl	1 hr.	.430	.012	.057	0.035	.534	-0.68
	24 hrs.	.390	.012	.045	.039	.486	0.28
	1 wk.	.370	.013	.043	.033	.458	0.84
	2 wks.	.400	.014	.068	.047	.529	-0.58
	4 "	.410	.013	.060	.036	.519	-0.38
	8 "	.390	.014	.060	.035	.698	0.02

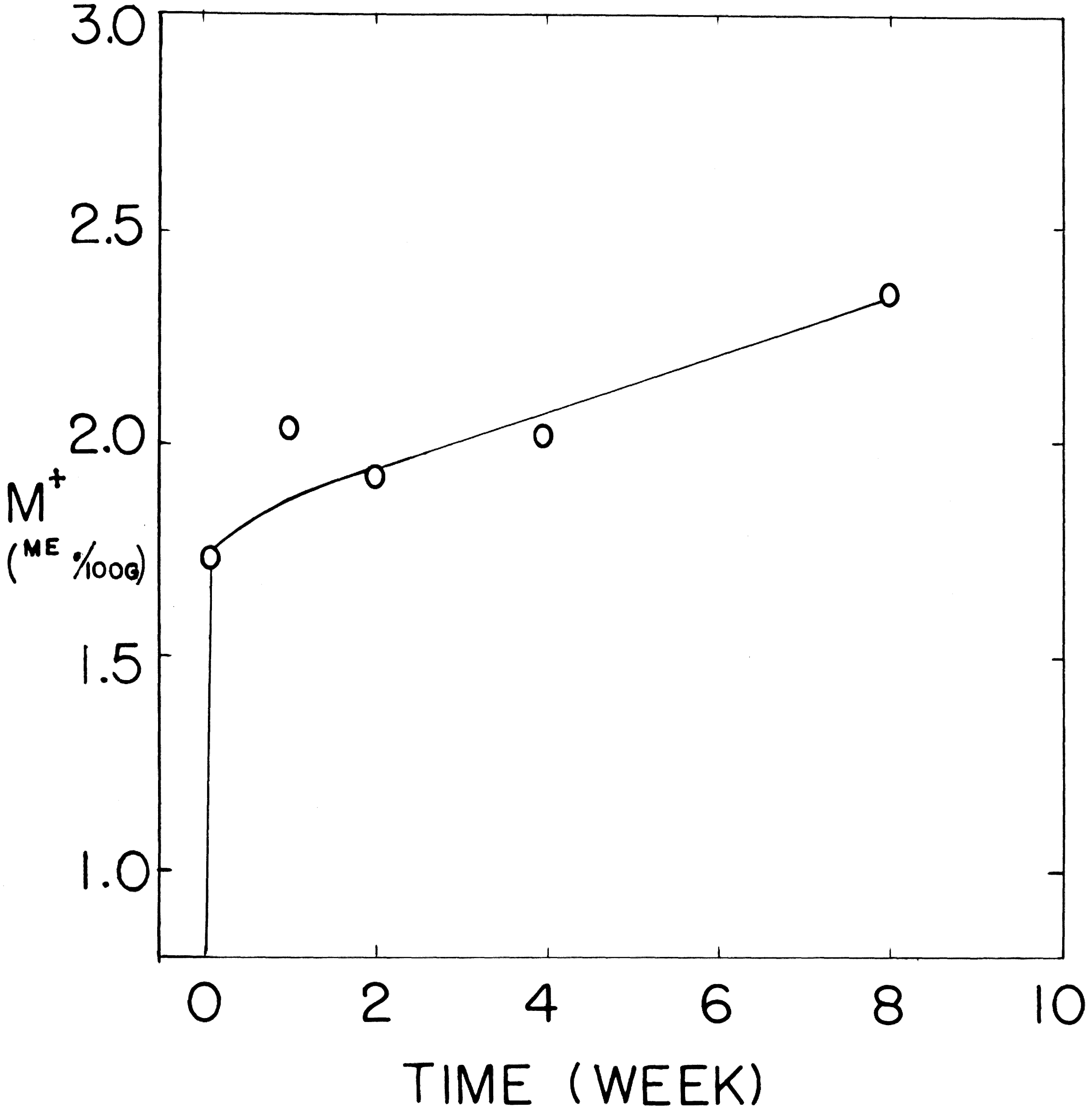


Figure 4. The effect of time on the disappearance of cations from 100 ml. of 0.01 N K_2SO_4 solution added to 5 gm. of Dixie Cecil soil.

time periods of one hour up to two weeks. The pH of the system was essentially unchanged (from pH 3.55 to 3.65). During the first week, the amount of conductivity decrease was less in the case of the Fe-kaolinite with an iron content of 51.93 $^{\text{m.mol.}}$/100 gm. clay than that with 81.47 $^{\text{m.mol.}}$/100 gm. clay. The difference, however, became smaller as the shaking time increased to two weeks. It appears that the conductivity continued to decrease slightly with a longer time of contact. The decrease of conductivity is assumed to be caused by the disappearance of electrolyte from solution and its adsorption by clay. During the first twenty-four hours the marked increase apparently is due to the adsorption of sulfate and the exchange of hydroxyl groups of the hydroxides or oxides of iron and aluminum combined with the rapid hydrolysis of exchangeable aluminum as a result of salt addition. (Ragland and Coleman, 1960) Increases with longer time probably were due to the slow hydrolysis of aluminum in the clay, which would produce a continuing supply of hydrogen ions, and is a rather slow reaction. The unchanged pH throughout the experiment appears to be due to the near equivalency of replaced hydroxyl ions and the hydrogen ions formed from hydrolysis. This reasoning was further borne out by a subsequent experiment, which was based on the assumption that the equivalents of anions in solution are equal to the equivalents of cations in solution. The results shown in Table 3 are obtained by taking the sum of the cations K, Ca, Mg, and Al in solutions of 0.01N K_2SO_4 or 0.01N KCl after each different time of equilibration with Cecil soil. Four different treatments were obtained by using two different volumes, 100 ml. and 50 ml., of each solution. The difference in total normality between the solution added and the equilibrium solution was assumed to be equal to the quantity of anions adsorbed by the soil.

The results obtained from adding 0.01N KCl to the soil gave erratic values for chloride adsorbed. This may be due partly to the fact that chloride is a weakly adsorbed anion. Under conditions of this experiment, no correlation was found between time and the quantity of cations present in solution. Upon the addition of 0.01N K_2SO_4 solution to Cecil soil, the quantity of cations present in solution was decreased with time, which indicated that anions held by the soil increased from 0.42 to 2.36 me/100 gm. and from 1.61 to 2.32 me/100 gm. soil for 100 ml. and 50 ml. solutions added to 5 gm. of soils, respectively. Soil with an addition of 50 ml. of solution had a much higher increase in adsorption within the first hour than did the same amount of soil with 100 ml. of solution added. The marked difference may be due to an error in the analysis. Cations in solution which decreased with increasing time were K and Al. When 100 ml. of K_2SO_4 solution was added, the decrease of K was from 0.845 to 0.79 me/100 ml. and that of Al was 0.078 to 0.036 me/100 ml. When 50 ml. of solution was added, Al was changed from 0.0305 to 0.0141 me./50 ml. The other cations remained essentially the same.

A plot of the amount of SO_4 retained in soil vs time taken from the cation summation data is shown in Figure 4. A rapid rise in the amount of cations retained in soils with the first 24 hours agrees with the previous experiments.

The disappearance of aluminum from solution suggests that hydrolysis of exchangeable aluminum occurred. Thus, the replacement of hydroxyl groups from the iron hydroxyl groups results in the neutralization of hydrogen ions from the hydrolysis of exchangeable Al which keeps the system from rising in pH, and makes the reaction proceed to completion. The overall reaction is described as:

$$K^+ + \text{Al-Clay-} \xrightarrow{H_2O} Al_x\,(OH)_y\ {}^{K}Y\text{-Clay} + y\ H^+$$

$$SO_4^{=} + R_x(OH)_y\text{- Clay} \longrightarrow R_x(OH)_{y-z}(SO_4)_z\text{- Clay} + z\ OH^-$$

In the case of conductivity determinations, the pH of the system was essentially unchanged, but the above mechanism would account for a pH drop or rise as well. All three observations have been made.

III. The Effect of pH on Anion Elution Curves

Typical elution patterns for Cl^-, NO_3^- and $SO_4^{=}$ ions at two pH values are shown in Figure 5, 6 and 7. The patterns were obtained by adding small volumes of 0.2N KCl, KNO_3 or K_2SO_4 solutions to columns containing a Cecil soil-cellulose powder mixture and following with H_2O. In general the curves are skewed towards the right. The lack of symmetry may be due partially to lack of equilibrium or other experimental errors. The long tails found at the lower pH values, however, are largely a result of anion retention by the soil. As the pH is decreased the anion peak is diminished and the tail grows longer. Similar results for Cl^- and $SO_4^=$ with a North Carolina Cecil soil were found by Berg and Thomas (1959).

According to chromatographic prediction, the position of the anion peak would be expected to shift to a higher volume as the affinity of the soil for the anion increased. The results in Figures 5 through 7 and those of Berg and Thomas (1959) suggest that there is a range of affinities found at any given pH. The anions which are eluted at a normal column volume are not held by the soil, whereas those which make up the tail are held with varying degrees of tightness. Chloride and NO_3^- (Figures 5 and 6) appear to be only loosely held at moderately low pH values; $SO_4^=$ exhibits a long tail even at pH 6.9 and has virtually no peak at pH 4.05.

It should be emphasized that the shape of the elution curves will depend not only on the soil and pH of the system, but also upon the amount of salt added. If enough salt is added the effect of anion "hold-up" will be negligible, whereas, the addition of very small amounts may result in a complete loss of the anion from solution. In these experiments a rate of 0.5 me./100 gm. soil was used, which would approximate a heavy application of potassium fertilizer.

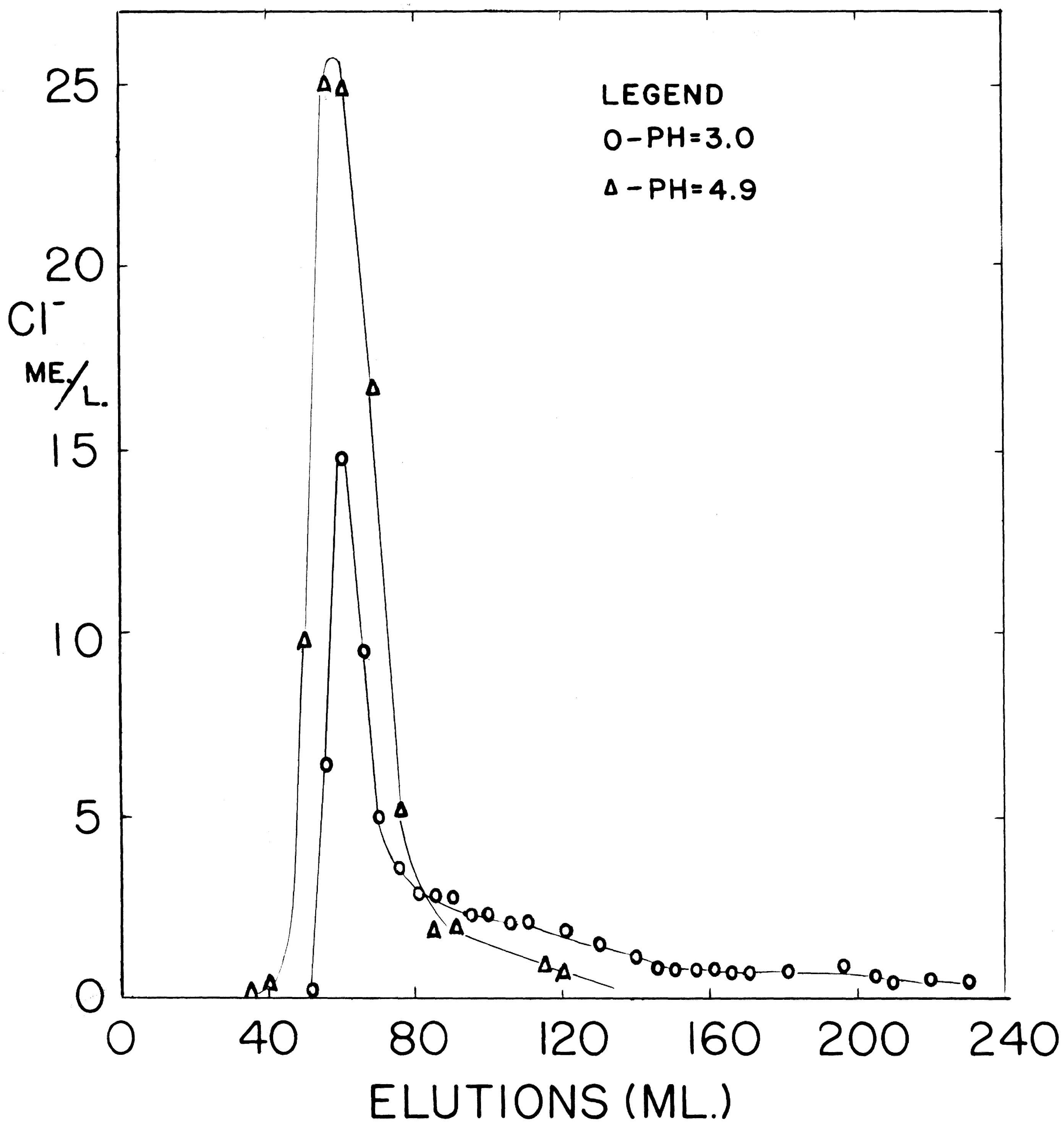


Figure 5. Cl⁻ Elution patterns for Cecil Soil at two different pH's.

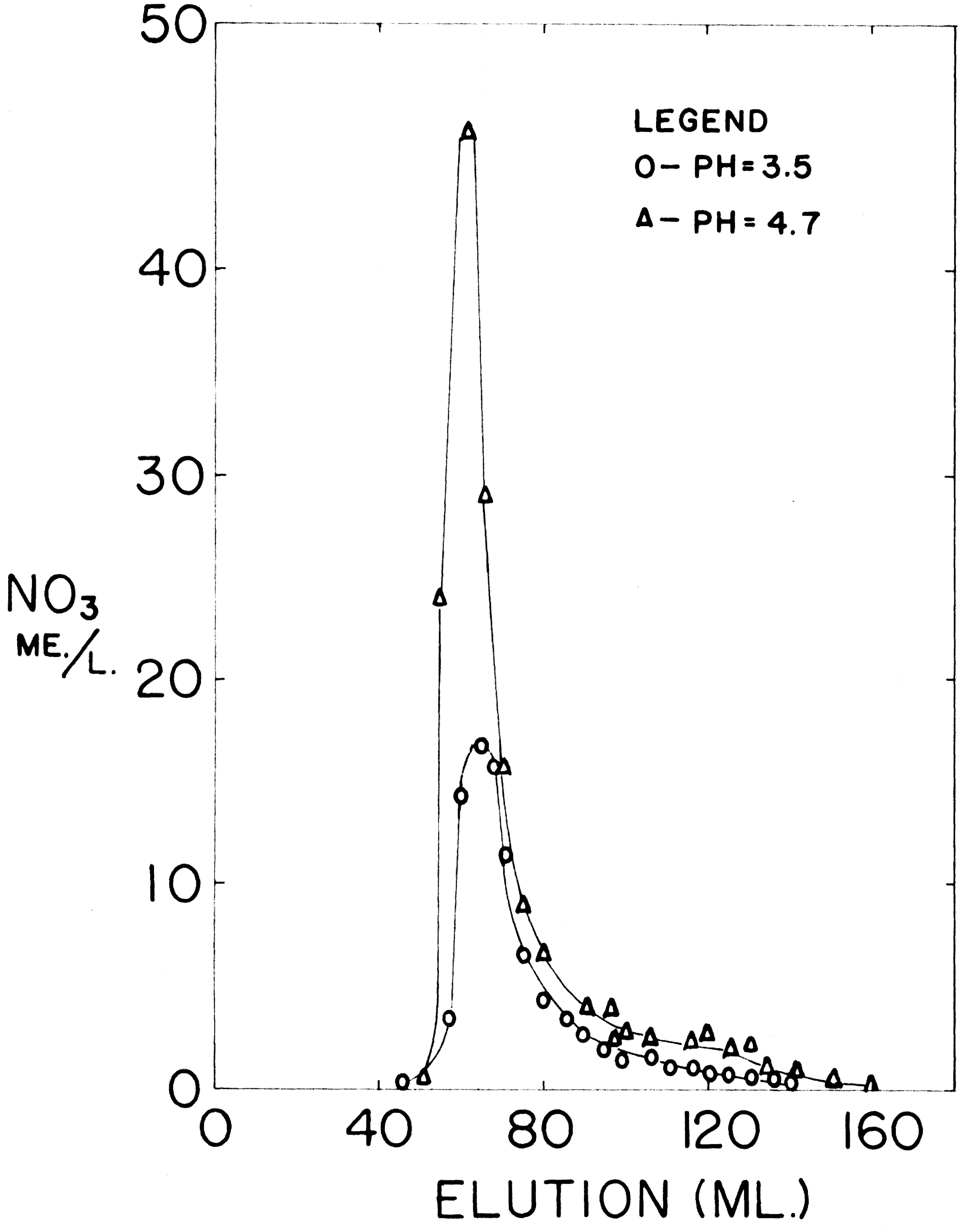


Figure 6. NO_3^- Elution patterns for Cecil Soil at two different pH's.

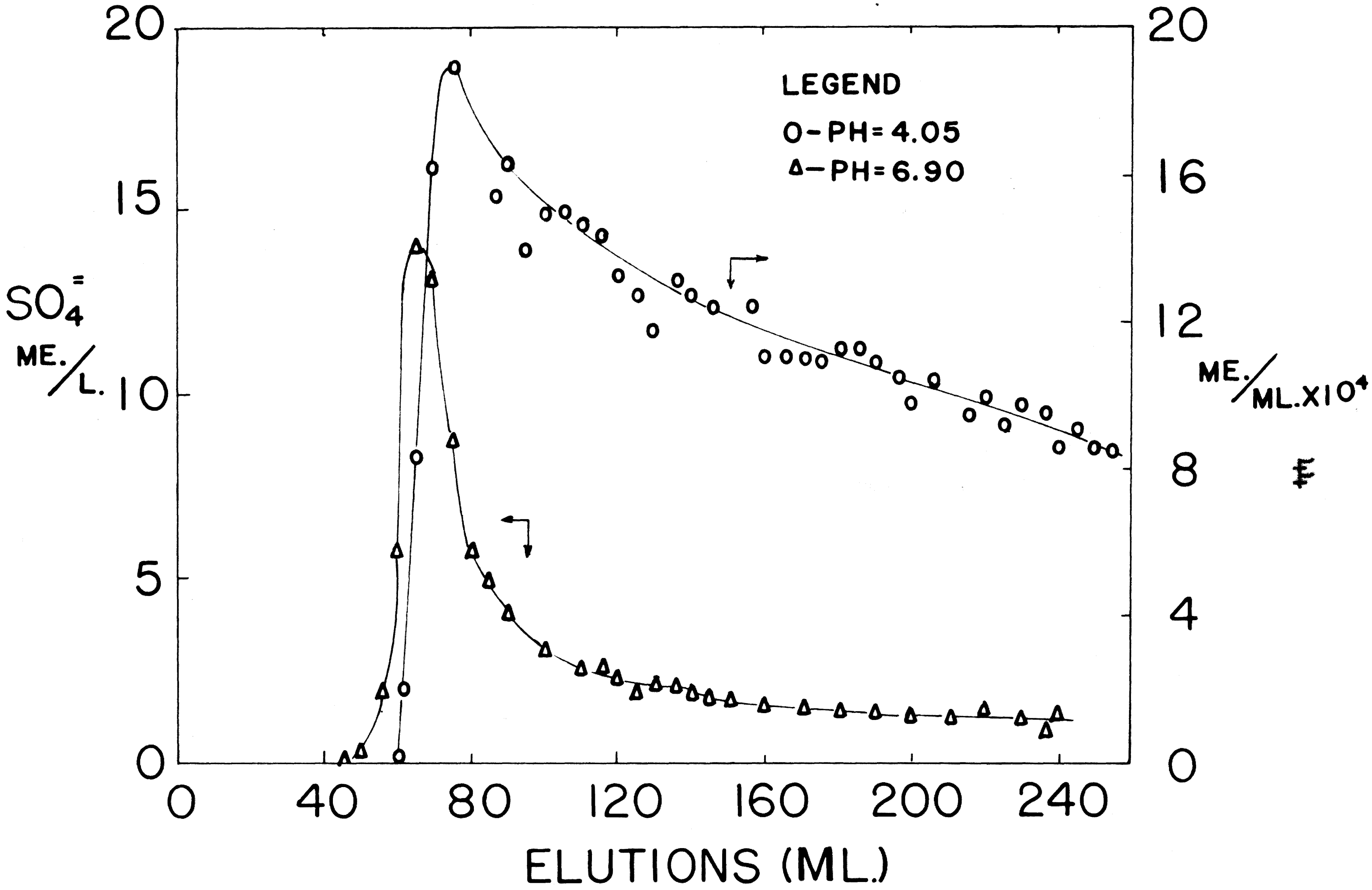


Figure 7. $SO_4^=$ Elution patterns for Cecil Soil at two different pH's.

Since the elution peak itself did not shift with pH reduction (c.f., Berg and Thomas, 1959) it was decided that a corrected peak volume, calculated at the point where half of the salt had been eluted, would be useful in estimating the effect of pH on the retention of anions in columns. Using the relation (Ketelle and Boyd, 1947)

$$Kd = \frac{(V-I)}{\rho} E$$

distribution coefficients (Kd's) for Cl^-, NO_3^- and $SO_4^=$ were calculated at a number of different pH values. The value for V was calculated from the ratio ml. H_2O needed to elute half the salt / ml. H_2O needed to saturate the column. E and ρ are the void fraction of the column and effective density of the exchanger. Data for all columns and sample calculations are given in the Appendix.

A plot of Kd vs pH for Cl^- and NO_3^- in Cecil soil is given in Figure 8. The approximately linear scattering of points shows no clear distinction between Cl^- and NO_3^- retention. This suggests that NO_3^- behavior can be predicted with confidence from Cl^- data. A very close relation between Cl^- and NO_3^- behavior in an acid, red soil also was found by Thomas (1960) using a different technique. Figure 9 shows a similar plot for $SO_4^=$ Kd's in Cecil soil. It is apparent that not only are the Kd values for $SO_4^=$ generally higher than Cl^- or NO_3^- Kd's, but also that there is a much sharper rise in Kd with reduced pH. Again an approximately linear relationship obtains, at least up to approximately pH 6.

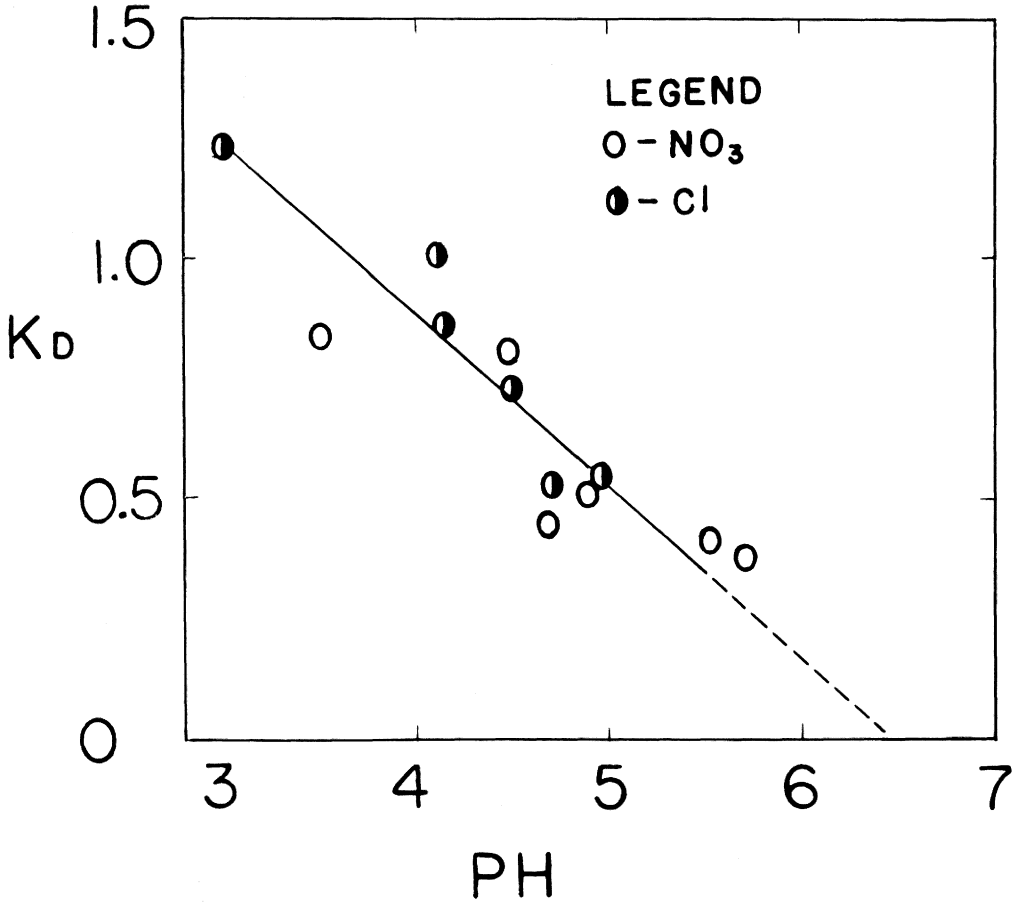


Figure 8. The effect of pH on the distribution coefficient of NO_3 and of Cl, in Dixie Cecil Soil.

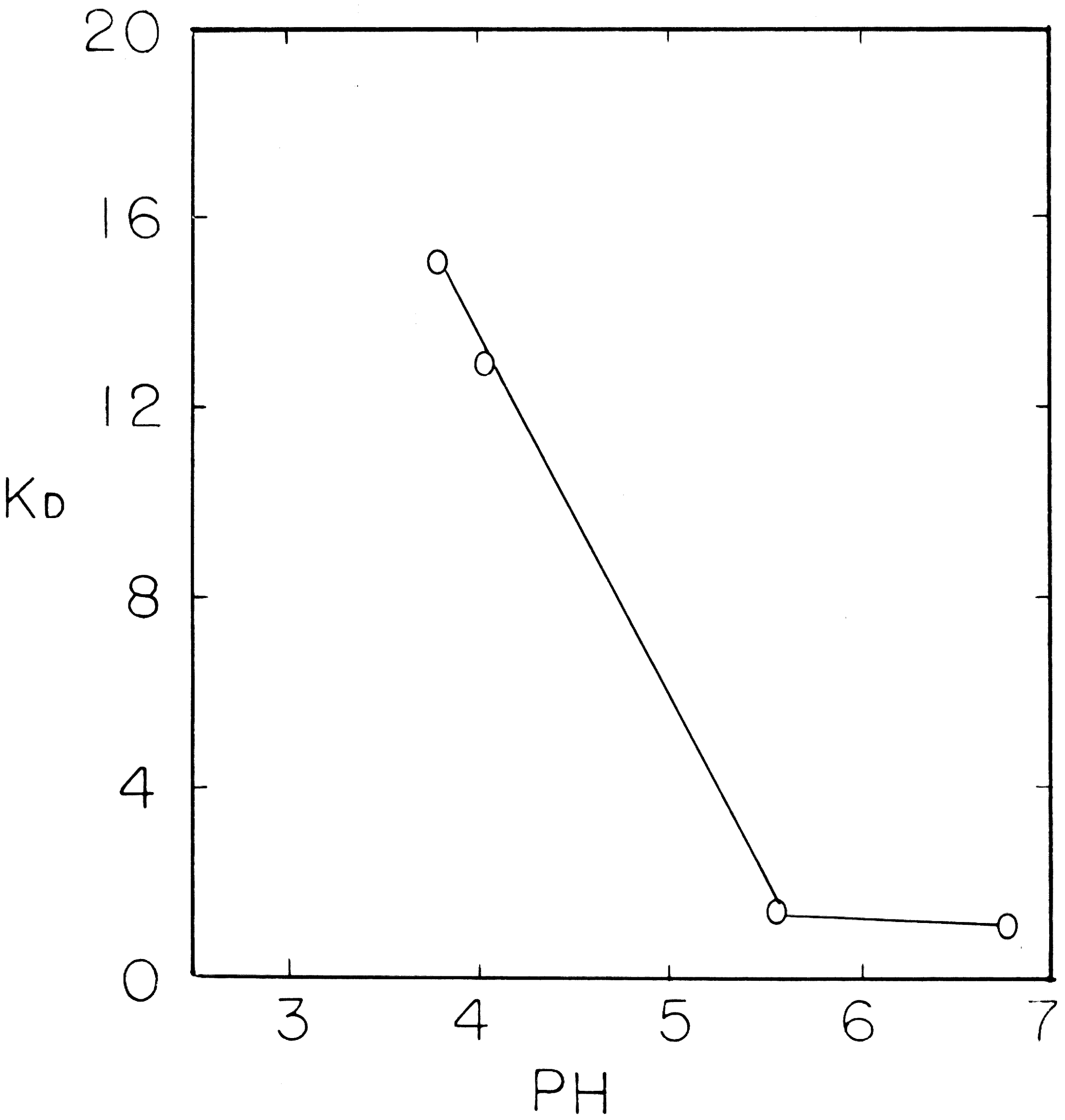


Figure 9. The effect of pH on the distribution coefficient of sulfate in Dixie Cecil Soil.

The pH vs. Kd interaction between Cl^- or NO_3^- and $SO_4^=$ suggests that equilibrium plots of relative affinities of anions, such as the one in Figure 1, would be altered drastically by pH. At a pH just below 6.0, Cl^- would be nearly as strongly held as $SO_4^=$; whereas, at a pH of 3.0 Cl^- would hardly be competitive with $SO_4^=$. More data on this effect are needed.

The reason for the linear relation between pH and anion retention is not clear, but it has been reported by other workers (Toth, 1937). The values for Kd reported here must be regarded at only relative numbers due to the factors mentioned above, but they suggest that salt movement under field conditions can be predicted reasonably well, even in soils which retain anions. The high values for Kd with $SO_4^=$ raise the question of sulfate availability under such conditions. Thus far, no definitive experiments on sulfate absorption by plants under such conditions have been reported.

SUMMARY AND CONCLUSIONS

Soil columns were used to study some factors that affect anion retention. Anions studied including chloride, nitrate and sulfate. The adsorbents were Dixie Cecil clay or soil, or Fe-kaolinite.

The retention of sulfate and chloride in Cecil clay was obtained using mixtures of 0.01N, K_2SO_4 and KCl to elute the soil column until apparent equilibrium was reached. The column then was analyzed for adsorbed chloride and sulfate. Chloride retained was nearly constant with a value of approximately 0.4 me./100 g. clay up to the mixture which was 90 percent KCl, where a much higher value of 1.90 me./100 gm. clay was obtained. The retention of sulfate was increased with an increasing amount of sulfate present in the mixture. When the proportion of sulfate was higher, apparent equilibrium was reached much more quickly. The "apparent" equilibrium gave rather low values of total anions retained, suggesting that the amount of anion retention is dependent upon time.

The time effect on the retention of anions was investigated by shaking 0.01N K_2SO_4 solution with Cecil soil, or clay for different time periods, using S^{35} as a tracer. The amount of sulfate left in the supernatant liquid was obtained; it indicated an increase of sulfate retention with the increase of time from five minutes up to four weeks. Similar results also were found by measuring the conductivity of the supernatant liquid obtained from 0.02N K_2SO_4 and iron-treated kaolinite shaken for from one hour up to two weeks.

Since S^{35} equilibrium can include isotopic exchange and a conductivity method carries many assumptions, the time effect on anion retention was further studied by assuming that the equivalents of cations in solution are equal to the equivalents of anion in solution. No increase in retention with time was found when KCl solution was added, but an increase was shown where K_2SO_4 solution was used with time periods ranging from one hour up to eight weeks.

The elution patterns were obtained by adding a small amount of 0.02N KCl, KNO_3 or K_2SO_4 to the top of a soil column and following it with distilled water. The effluent was collected in fractions and analyzed for chloride, nitrate or sulfate respectively. Results showed that less water was needed to recover one half of the anion added at higher pH and more was required at lower pH values. The elution patterns were non-symmetrical with long tailing edges at lower pH values, and particularly in the case of sulfate.

Anion retention as affected by pH was estimated by distribution coefficients (Kd's) which were calculated by using the equation of Ketelle and Boyd, (1947). The value for hold-up volume was taken where one-half of the salt was replaced. Distribution coefficients decreased linearly with an increase in pH. Sulfate gave Kd values higher than those for chloride and nitrate which were similar to each other.

From the above observations, it is concluded that (1) Chloride is held much less tightly by soils than is sulfate.
(2) Using a strongly retained anion such as sulfate, it apparently takes longer to reach true equilibrium, indicating the existence of a time factor in anion retention.
(3) Sulfate retention by soils is positively correlated with time. More is retained after longer periods of contact. The continuing hydrolysis of aluminum is suggested as the cause of the time effect. Such hydrolysis produces hydrogen ions which can neutralize the hydroxyl ions exchanged by anions, this keeps the pH of the system from going up, and continues the reaction.
(4) The non-symmetry of elution patterns indicates the retention of anions. The longer the tail, the more tightly the anions are retained.
(5) Distribution coefficient values for Cl^-, NO_3^- and $SO_4^=$ salts of K^+ showed an approximately linear relation between pH 3 and 6. Chloride and NO_3^- gave similar Kd values, whereas SO_4 was held much more tightly at low pH.

APPENDIX

A. Anion Elution Data:

Table 1 Quantities of anion in each five ml. fraction of the eluted solutions: (me./ml. x 10^3)

Fraction number	Cl^- pH						NO_3^- pH		
	3.0	4.1	4.1	4.5	4.7	4.9	3.5	4.5	4.7
1	0	0	0	0	0.1	0.1	0	0	0
⋮					0.1	0.1	0	0	0
9	0		.1	0.2	0.1	0.1	0	0.03	0.27
10	0		.1	0.2	0.4	1.0	0.62	0.08	0.61
11	6.4	0	1.6	0.2	14.9	25.0	3.23	2.82	24.19
12	14.9	6.1	12.4	6.7	25.1	25.0	14.52	43.15	46.77
13	9.6	14.6	12.6	16.4	19.2	16.8	16.94	41.94	29.44
14	5.0	11.3	8.0	12.7	9.3	4.2	11.29	24.19	15.32
15	3.7	7.2	5.5	8.5	5.3	4.4	7.26	14.11	9.27
16	3.1	5.4	4.0	5.4	3.2	2.4	4.68	8.71	6.61
17	3.0	3.4	3.0	4.2	2.5	2.3	3.71	7.42	4.03
18	3.1	3.3	3.3	4.2	2.2	--	3.23	6.85	4.19
19	2.5	2.9	3.1	3.4	1.7	--	2.34	4.47	4.00
20	2.6	2.5	--	2.9	1.3	--	2.15	4.79	3.44
21	2.3	2.2	2.2	2.5	1.2	--	1.91	4.24	2.63
22	2.3	2.1	1.9	--	1.0	--	1.69	3.87	1.96

Table 1 (Continued)

Fraction number	Cl^- pH 3.0	4.1	4.1	4.5	4.7	4.9	NO_3^- pH 3.5	4.5	4.7
23	--	1.9	1.3	1.5	1.0	1.1	1.51	3.34	2.15
24	2.2	1.7	--	--	1.0	0.7	1.37	3.11	2.37
25	--	1.6	--	--	0.8	--	1.21	2.90	2.15
26	1.8	1.6	1.4	--	0.8	--	1.18	2.63	0.54
27	--	1.4	1.0	--	0.6	--	1.05	2.42	0.83
28	1.4	1.4	1.0	0.8	0.6	--	1.02	2.19	0.65
29	--	1.2	--	--	0.6	--	0.89	2.13	0.80
30	--	1.2	--	--	0.6	--	1.08	1.81	--
31	--	1.0	--	--	0.6	--	0.91	--	--
32	1.1	1.0	--	--	0.6	--	0.86		
33	--	1.0	--	--	0.6	--	0.81		
34	1.0	1.0	--	--	0.5	--	0.70		
	0.403	0.395	0.398	0.409	0.395	0.360	0.414	0.368	0.383
	0.146	0.142	.142	0.144	0.147	0.147	0.142	0.142	0.145
	$\frac{80}{55.2}$	$\frac{77.5}{55.8}$	$\frac{73}{56}$	$\frac{71.1}{56.9}$	$\frac{64.4}{53.65}$	$\frac{61}{50}$	$\frac{75}{58.2}$	$\frac{68}{51.7}$	$\frac{61.84}{52.7}$
K_d	1.24	1.08	0.85	0.71	0.52	0.54	0.84	0.81	0.46

Fraction Number		NO_3^- pH			$SO_4^=$ pH		
	4.9	5.55	5.7	3.8	4.05	5.6	6.9
1	0	0	0	0	0	0	0
⋮							
9	0	0	0	0	0		
10	0.03	0.05	1.21	0	0		0
11	3.23	18.45	42.74	0.17	0	0	1.90
12	46.77	68.50	78.87	0.11	0	2.55	5.69
13	41.94	56.05	46.77	0.12	0.82	16.33	14.07
14	24.19	24.60	23.39	0.27	1.63	12.54	13.28
15	12.70	13.31	14.11	0.49	1.90	8.28	7.87
16	8.06	9.03	6.34	0.73	1.79	5.89	5.61
17	6.45	6.29	3.82	0.85	1.53	4.92	4.83
18	4.35	5.56	2.95	0.94	1.64	4.29	3.92
19	0.97	4.67	1.69	0.99	1.39	3.43	3.56
20	0.27	4.24	1.13	1.06	1.52	3.50	3.12
21	3.11	3.87	0.65	1.12	1.49	3.19	2.88
22	2.55	3.23	0.45	1.12	1.47	2.72	2.50
23	0.13	1.89	0.73	1.19	1.43	2.64	2.58
24	0.14	1.82	0.81	1.13	1.22	2.48	2.26

Fraction Number	NO_3^-			$SO_4^=$			
	pH			pH			
	4.9	5.55	5.7	3.8	4.05	5.6	6.9
25	0.13	1.56	0.81	1.33	1.15	2.45	1.98
26	0.22	1.26	0.81	1.27	1.07	2.26	2.00
27	0.08	1.02	0.16	1.14	1.21	2.03	2.01
28	--	0.73	--	1.07	1.19	1.92	1.86
29	--	0.48	--	1.05	1.15	1.79	1.80
30	--	0.26	--	0.98	1.09	1.86	1.68
31	--	0.13	--	0.99	1.15	1.65	1.63
32	--	--	--	1.06	1.02	1.81	1.54
33	--	--	--	1.01	1.00	1.59	1.27
34	--	--	--	1.02	1.01	1.60	1.39
35	--	--	--	1.05	0.98	1.41	1.33
36	--	--	--	0.95	1.03	1.44	1.35
37				0.89	1.03	1.31	1.27
38				0.76	0.98	1.18	1.15
	0.397	0.392	0.379	0.383	0.397	0.397	0.404
	0.143	0.140	0.140	0.135	0.146	0.144	0.140
	$\frac{65.9}{55.6}$	$\frac{64.4}{56.1}$	$\frac{61.88}{54.2}$	$\frac{362}{56.8}$	$\frac{312.5}{54.2}$	$\frac{84.5}{55.2}$	$\frac{82}{57.8}$
K_d	0.52	0.42	0.38	15.24	12.96	1.47	1.19

B. Sample Calculations:

1. Equation $$K_d = \frac{(V-1)\,E}{\rho}$$

Where K_d = distribution coefficient

= fraction of void space

= density of soil column

= volume of solution needed to displace one-half of the anion added.

2. Calculations of K_d:

Cl at pH 3.0	NO_3 at pH 3.5	SO_4 at pH 6.9
$\frac{(\frac{92.5}{55.2} - 1)(0.403)}{(0.146)}$	$\frac{(\frac{75}{58.2} - 1)(0.414)}{(0.142)}$	$\frac{(\frac{82}{57.8} - 1)(0.404)}{(0.140)}$
K_d = 1.87	K_d = 0.854	K_d = 1.19

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ABSTRACT

FACTORS EFFECTING ANION RETENTION IN SOILS

The purpose of this investigation were to use chromatographic methods to study the effects of pH, time of equilibration, and the effect of anions themselves in the anion retention in an acid red soil.

It was found that chloride was held much less tightly than sulfate by soils. It was also noted that more sulfate was retained at higher concentration.

A time factor was also noted in this investigation. It took a longer period to reach true equilibrium when sulfate was used. Results showed a positive correlation between sulfate retention and time to reach true equilibrium. The disappearance of aluminum from the solution added to soil suggested that the continuing hydrolysis of aluminum being the main cause of the time effect. Such hydrolysis produces hydrogen ions which can neutralize the hydroxyl ions exchanged by anions and kept the pH of the system from going up and continuing the reaction.

The non-symmetrical elution patterns indicated the retention of anions, The longer the tail of the elution patterns, the more tightly the anions are retained.

Distribution coefficients (Kd) for Cl^-, NO_3^- , and $SO_4^=$ showed approximately linear relationships between pH 3 and 6.

Chloride and NO_3^- exhibited similar Kd values at similar pH values. It also indicated that $SO_4^=$ was held much more tightly at low pH values.