

FIXATION OF ALUMINUM-HYDROXIDE (HYDRATED OXIDE)
INTERLAYERS IN SOME OKLAHOMA SOIL CLAYS

By

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Thesis Approved:



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CHAPTER I

INTRODUCTION

One of the most intensive areas of research in soil chemistry and clay mineralogy in recent years has been the study of mechanisms responsible for the occurrence of aluminum interlayers in 2:1 type layer clay minerals. This mechanism may be important in understanding the chemistry of soil phosphorus solubility, ammonium fixation, cation exchange capacity, acidity, alkalinity, clay surface area and shrink-swell. These factors in soils are supposedly related to the character of the soil clay interlayer.

It is believed that the source of aluminum interlayers in soil clays resulted from the decomposition of aluminosilicate minerals and the solubilization of aluminum from parent rock by the action of a very dilute sulfuric or other acid solution. The magnitude to which aluminum interlayers occur in soil clays increases with proximity to the surface and the soil usually exhibits a low cation exchange capacity. Weak acid conditions, low organic matter and the nature of the parent material are among the most important factors which govern the abundance and occurrence of aluminum interlayers in soil clays.

Present concepts convey the idea that aluminum interlayers are responsible for soil acidity and also act as clay preservatives. Clay minerals may acquire aluminum interlayers as a result interlamellar penetration which causes replacement of other exchange cations. Such

a reaction provides the clay with interlayers more soluble than the octahedral aluminum layer and thus prevents further destruction of the 2:1 lattice structure.

The first objective of this study was to investigate hydroxy-aluminum polymer fixation by the use of $\text{Al}_2(\text{SO}_4) \cdot 18\text{H}_2\text{O}$ and NaOH . Because sulfate ions usually occur in soils and in large amounts, it is believed that the solubilization of aluminum in the parent rock was caused by the action of a very dilute sulfuric acid solution.

The clays in soils and parent shales of the southwestern part of the United States have been exposed to dilute sodium aluminum sulfate solutions sufficiently long enough to have reached equilibrium with the soil solution. Therefore, a correlation between the amount of aluminum hydroxide (hydrated oxide) polymers against known hydroxy-aluminum solutions should exist. This correlation should allow us to predict the type of weathering or synthesis process that these clays have been exposed to and the translocation and deposition of weathering products.

A second objective of this study was to investigate the ability of clays, with no interlayers, to fix artificial aluminum interlayers. Further study will include an attempt to explain why coarse clays fix more aluminum interlayers than fine clays. Recent studies conducted by various soil chemists and clay mineralogists reported that hydroxy-aluminum polymers can be prepared artificially and introduced into clay interlayer spaces. This reaction usually causes clay minerals to exhibit basal spacings of $14\overset{\circ}{\text{A}}$, low CEC, and reduced shrinkage and swelling.

It is believed that the type of clay mineral, degree of layer charge, bonding strength of the clay layer structure and clay particle

size are the factors to be considered for maximum artificial aluminum interlayer fixation. The data presented in this thesis will increase our knowledge of alumino-silicate formation and provide a better understanding of clay mineral characteristics.

CHAPTER II

LITERATURE REVIEW

Occurrence and Importance of Aluminum Interlayers in 2:1-2:2 Type Layer Silicates. Soil chloritization is defined as the formation of aluminum interlayers in the interlayer spaces of 2:1-2:2 type layer silicates. The appearance of aluminum interlayers in vermiculite and montmorillonite is believed to contribute to an increasingly stable $14\overset{\circ}{\text{Å}}$ spacing which is a diagnostic characteristic of chlorite. In this respect, aluminum interlayers may be considered as unstable forms of chloritic material which is deposited in the interlayer spaces of clay minerals during weathering. The first aluminum interlayer was reported by Brown (4) in a stable dioctahedral vermiculite in some soil clays in Great Britain. Since that time, numerous examples of stable minerals with $14\overset{\circ}{\text{Å}}$ spacings and interlayer aluminum have been reported by (37, 16, 28, 47, 39). Jefferies (q6) observed a similar mineral in the surface horizon of two soil clays and referred to it as "Chloritic-like" material. Sawhney (30) reported that the degree of chloritization in layer silicates may be measured by cation exchange determination after interlayer extraction. Sawhney (41) showed that an intensive treatment of a particular clay by various interlayer extraction methods did not cause an increase in basal spacings from 14 to $18\overset{\circ}{\text{Å}}$. This identifies a mineral as vermiculite with aluminum interlayers. Aluminum interlayers inhibit the expansion of montmorillonite from a 14 to $18\overset{\circ}{\text{Å}}$ and also resist

contraction of both vermiculite and montmorillonite from 14 to 10Å on K-saturation and heating to 100° C.

An interlayered montmorillonite will resist expansion when Mg-saturated and ethylene glycol solvated and also resists collapse when K-saturated and heated to 100° C. Temperatures above 500° C. usually cause collapse and a resultant 10Å⁰ peak due to dehydroxylation of the aluminum interlayer polymer structure.

Sawhney (40) believed that aluminum-interlayers occurred in soils as essentially chloritization of the expanding 2:1 type layer silicates, and are probably comprised of hydrated polymers of $Al(OH)_2^+$ ions which are most abundant at a pH of 5. Jackson (22) stated that the release of aluminum from 2:1-2:2 type layer silicates in soils occurs at a rate which is required for abundant aluminum interlayering. This acidic cation is ascribed as aluminohexahydronium which has a greater acid strength than the common weathering acid, H_2CO_3 . Jackson (22) also reported that the chemical weathering relationship of acid soils makes it clear that interlayer precipitation of $Al(OH)_3$ gel in expansible layer silicates tends to occur preferentially to precipitation of a separate free gibbsite phase. This is analogous to saying that crystalline gibbsite does not precipitate within the interlayer spaces. The argument used to support this theory is based on two lines of evidence: (a) clays interlayered with the so-called "aluminum polymers" occur widely in both acidic and alkaline soils, (b) additional absorption of aluminum from solution by aluminum saturated montmorillonite (with a concomitant lowering of pH, which signifies hydroxy-aluminum polymerization), occurs at a K_{sp} less than that of gibbsite. The selective accumulation of exchangeable aluminohexahydronium ions in the interlayer spaces of

expansible layer silicates causes polymeric hydroxy-aluminum precipitation. This occurs while the K_{sp} in the equilibrium solution is approximately equal to or slightly less than that of free gibbsite. This again supports the idea that gibbsite precipitation does not occur within the clay interlayer spaces.

Jackson (22) surmised that layer silicates serve as templates for interlayer polymerization and that aluminum released by weathering tends to be deposited in 2:1-2:2 intergrades with aluminohexahydronium interlayers rather than gibbsite. These layers may also serve as negatively charged surfaces for adsorbing the positively charged OH-ion units. A classical example of this was noticed by Nagelschmidt (33) in some red-yellow podzolic soils in the southeastern United States. These soils were derived from mica schist which developed aluminous interlayers and weathered further to yield kaolinite. No detection of gibbsite appeared while weathering occurred in this particular case, but it has been observed in the weathering of basic rocks. Bates (2) reported that the common end products of the weathering processes of basic igneous rocks of Hawaii are gibbsite, goethite, anatase and ilmenite. The intermediate state of these clay mineral are halloysite and iron montronite. No detections of mica or kaolinite appeared in the weathering products of these basic igneous rocks. His conclusion was that micaceous minerals could only be formed by weathering of granitic potassium feldspars. Gibbsite occur in some soils and not in others. An explanation for this has been attempted by Jackson (22), who postulated that the presence of expansible layer silicates in soils is responsible for the absence of gibbsite. No gibbsite occurs when the interlayer precipitation of alumina prevents the K_{sp} of free $Al(OH)_3$ from being reached in the

matrix solution. Such a process is ascribed to an "anti-gibbsite effect" in chemical weathering.

Schwertmann and Jackson (43) reported that both vermiculite and montmorillonite have the ability to produce hydrolysis and polymerization of aluminum in the presence of exchangeable aluminum. They reported that this aluminum is liberated from the structure when attacked by exchangeable hydronium and that the non-exchangeable hydroxyl aluminum formed exhibits a third buffer range. These ions which are weathered from the terminal edges of the clay mineral 2:1 layer structure are solubilized by a trace to several hundred parts per million of sulfate ions. Aluminum as a part of the complex sodium or magnesium aluminum sulfate is quickly moved to the basal oxygen planes of the mineral and deposited where it is polymerized with other hydrated oxides of aluminum. These hydrated aluminum oxide polymers serve as preservative of the clay mineral with resultant reduction in cation exchange. The preservation effect is due to: (1) replacement of other cations by positively charged aluminum polymers; (2) general protection of the 2:1 lattice by providing an interlayer more soluble than the octahedral layer; and (3) a source of aluminum for reacting with lattice destructive phosphates. Harrison and Murray (13) found that clays are more weathered in the upper horizons than in the lower horizons. Clay found in the surface contained a mixed layer of aluminum-silicate heavily interlayered with aluminum hydroxide polymers. They noted several x-ray diffraction peculiarities of the clays such as; asymmetry of the 001, broadening of the 002, and asymmetry of the 003 reflection toward the high angle side. These effects are characteristic of interlayering with aluminum hydroxide polymers. They reported that the weathering

environment was acidic in nature and that potassium had moved out of the micaceous minerals, thereby allowing expansion followed by hydroxy-aluminum interlayering.

It has been speculated by (40, 22, 36) and others that vermiculite holds aluminum interlayers in its interlayer spaces more tightly than montmorillonite. It has also been suggested by Jackson (22), that the cation exchange sites are more closely concentrated in expansible $14\overset{\circ}{\text{A}}$ minerals than in swelling intergrades and provide a more extensive and stable exchange site. This causes a greater extent of covering by positively charged aluminum interlayer groups which appears to result in polymerization of aluminum into hexa-aluminohydroxyhydronium units. These units appear as polymers of $\left[\text{Al}_6 \text{ OH}_{12} \text{ -OH}_{12} \text{ }^{6+} \right]$ and larger, which deposit in vermiculite and montmorillonite interlayer spaces.

Since vermiculite has its characteristic $14\overset{\circ}{\text{A}}$ spacing (001), the positively charged polymers can attach to both surfaces, and the interlayer positive (+) proximity to the negative (-) charge of the layers is closer than that for swelling intergrade. As a result, less extensive interlayer building is necessary in vermiculite than montmorillonite for a drastic cation exchange decrease. It is believed by Jackson (22) that since the layers of vermiculite have a higher negative charge due to a greater amount of isomorphous substitution in the silica tetrahedra, the positively charged aluminum polymers have a greater affinity for these sheets and provide greater interlayering. Frink (11), reported that soils that contain an abundance of interlayered aluminum such as vermiculitic soils usually undergo the largest loss in cation exchange, contain the most citrate extractable aluminum and suffer the largest weight loss on extraction.

Magnitude and Stability of Aluminum Interlayers. Aluminum interlayers have been found to be most abundant in soils derived from parent materials of granite, gneiss and micaceous schist. The stability of these interlayers is usually measured by the temperatures ($^{\circ}\text{C}$) required to cause complete collapse of a $14\overset{\circ}{\text{A}}$ basal spacing to $10\overset{\circ}{\text{A}}$. Rich (36) indicated that the extent of chloritization varies between soils derived from different parent materials. It was also stated by Rich that a soil's environment exerts a marked influence on its formation. A classical example of this has been observed by Nagelschmidt et al. (33) in some Highland soils. His reports showed that the mineralogy of a well drained soil was altogether different from that of a poorly drained soil in the same area. Analysis of these samples showed kaolin formation to be dominant in the poorly drained soils of that same region. Sawhney (41) found that the cation exchange capacity increased as much as 30-40% after interlayer-aluminum removal with the increase being more pronounced in well drained than in poorly drained soils. Rich and Obenshain (37) obtained similar results when $\text{KCl}+\text{KOH}$ or $\text{HCl}+\text{NH}_4\text{F}$ was used to extract the interlayer material from some stable $14\overset{\circ}{\text{A}}$ minerals.

They reported that after interlayer-aluminum removal, the samples collapsed to a basal spacing approaching $10\overset{\circ}{\text{A}}$. Tamura (47) extracted these aluminum-interlayers with N Na-citrate and reported similar results, but also observed a marked increase in cation exchange capacity from 72.3 to 115.6meq/100 grams. Dixon and Jackson (10) suggested that these interlayer groups can be removed by preheating 0.1 gm. samples to 400°C . followed by 2.5 minutes of boiling in 100ml of 0.5N NaOH. They reported similar results and postulated a more complete extraction of interlayer material than (37, 47).

Increases in cation exchange capacity following interlayer-aluminum removal have been shown by Sawhney (41) to be more pronounced in the upper horizons. This was attributed to the greater interlayering ability of the upper horizon in weak acid soils. Further study showed that clays from the B21 and A1 horizons in some cases did not collapse to a sharp 10\AA peak^o even after heating to 450°C . Further heating above 500°C did result in complete collapse of these minerals due to dehydroxylation of the interlayer polymer structure. This very well clarified the hypothesis that a greater intensity of weathering occurs near the surface thus releasing abundant amounts of aluminum ions. Since these ions are more abundant in upper horizons than in the lower horizons this explains the reason for greater interlayering and stability property of upper horizon clay aluminum interlayers as compared to lower horizons. Recent data reported by Sawhney (40), on a series of Holyoke and Wethers "Field soils of the northeastern United States", fully supported this theory. The data showed that 6 to 9 hours of citrate extraction was needed to extract the aluminum interlayers from the A1 horizon before a sharp 10\AA peak^o was observed. In contrast, only 3 hours of extraction was needed for extraction of the B2 horizon clays. This also supported the theory that aluminum interlayers and interlayer stability increases with proximity to the surface. After interlayer extraction, increases in spacing from 14 to 18\AA ^o have also been observed in some intergradient chlorite-montmorillonite. The expansion from 14 to 18\AA ^o could also result from a lowering of the layer charge by the aluminum extraction if some of the aluminum is pulled out of the tetrahedral or octahedral position. Dixon and Jackson (10) reported that removal of interlayer-aluminum leaves a defect in the clay structure,

which is probably compensated for by terminal hydroxyls on the silica tetrahedra. They also showed that aluminous interlayers found in coarse clays have greater heat stabilities than those in the more montmorillonitic or fine clay fraction. Sawhney (41) reported that the increase in cation exchange capacity is higher in clays where the interlayers are more stable. This was concluded after interlayer extraction and an increase in cation exchange from 35 to 37% was observed in stable upper horizons. This was compared to only a 15% increase in the less stable lower horizon of the same region. From these data, the conclusion was that since a higher cation exchange occurs after extraction in the highly chloritic clays, it is plausible that aluminum interlayers are, in part, responsible for the stability of the $14\overset{\circ}{\text{A}}$ (001) diagnostic spacing and reduced cation exchange as found in some soils.

In some Gloucester soils Sawhney (40) observed that aluminum interlayer production was completely inhibited due to a low pH and high organic matter content. The filling of clay interlayer spaces is believed by some soil chemists to be only partial and still others believe that these aluminum groups exist in sheets throughout the interlayer space.

Frink (11) postulated the theory of island polymerization. This is analogous to an atoll with a few islands in a central lagoon. Data which supported this theory is based on a recovery of 95% of the cation exchange capacity after only 2 hours of citrate extraction and concomitant collapse of the mineral to $10\overset{\circ}{\text{A}}$. Frink further hypothesized that these islands appear to be more concentrated near the edges of the clay sheets and, in fact, they must form an almost completely closed ring or fence which prevents smaller cations from entering the interlayer spaces. Aluminum continued to be extracted for at least 6 hours,

but only minute changes in cation exchange resulted. This indicated that all of the citrate-soluble aluminum is not contained in interlayer positions.

Results analogous to these have also been reported by Dixon and Jackson (10), while examining some Ap and A₂ horizons of Cookeville, Crosby and Tatum soils. They reported a reduction in glycerol retention relative to exchange capacity by aluminous interlayers. This also indicated a concentration of the hydroxy-aluminumhydronium (or allophanic) islands near the edges of the crystal plates, thus blocking entry of the large glycerol molecules while admitting the smaller exchangeable cations.

Soil Acidity as an Aluminum Hydrogen-Ion System. Extensive studies which have been made on cation exchange by soil chemists have been a substantial contribution to a better understanding of soil reactions in relation to acidity. One of the concepts emerging in recent years has been that of soil acidity as an aluminum-hydrogen ion system. In the late 1920's the concept that acid clays were hydrogen clays became well established, particularly in the United States. This concept later gave way to the current concept of soil acidity as an aluminum-hydrogen ion system. If we are to consider that soil acidity is actually ionized aluminum, then it becomes necessary to explain the mechanism by which aluminum ions provide the hydrogen or hydronium ions necessary to give low soil pH values. Jenny (27) discussed the possibility that the H⁺ ions are provided by hydrolysis on the surface of aluminum clays. Rich and Thomas (38) also considered hydrolysis as the mechanism by which hydrogen ions are supplied to the soil solution. This concept indicates that hydrolysis continues only if there are absorbents present to hold

the hydrolysis products. The results of such a reaction may be the formation of various hydroxy-aluminum compounds. A number of techniques were involved in the experiments which led to the relatively general acceptance of soil acidity as an aluminum-hydrogen ion system. Extractions revealed that acidity developed in the interaction between a hydrogen clay and neutral salt solutions. The clear salt extracts usually contain aluminum and ferrous ions which were directly exchanged for the cations of the added salt. The subsequent hydrolysis of the aluminum and iron salts gave rise to the acidity observed in the supernatant liquid. There are other opinions which seem to indicate that the replacement is one of hydrogen ions associated with neutral salts to give rise to free acid which then dissolves the aluminum and iron oxides present in the soil or clay. Differences in opinion also exist regarding the total amount of aluminum which can be displaced on the addition of neutral salts to hydrogen clays. Marshall and Paver (31) observed that there is a limit to the amount of aluminum ions which can be displaced from hydrogen clays by leaching with neutral salts. Brown and Kelly (5) found that aluminum ions are liberated as often as the clay is rendered unsaturated by leaching with dilute hydrochloric acid and then treated with neutral salts. Mukherjee et al. (32) found that at a given equilibrium pH, the amount of aluminum brought into solution by HCL constituted a small fraction of that liberated by $BaCl_2$. At a constant pH and concentration of barium solution, the amount of aluminum liberated increased as the pH of the hydrogen clay decreased along with increases in salt concentration. The relationship between these two reactions is illustrated by a curve that closely resembles an absorption isotherm. These data seem to indicate that aluminum ions are directly

exchanged for the cations of the added salts and not brought into solution by a secondary process. Marshall and Paver (31) indicated that unsaturated clays (clays which had been saturated by electro dialysis), are actually mixtures of aluminum-hydrogen clays. These findings apparently did not influence the prevalent concept of that time that acid clays were hydrogen clays. Mukherjee et al. (32), in their study of two soil clays, one predominately kaolinite; found that the replacement of cations with 0.02N HCL produced acidity in the supernatant solution. The total acidity displaced included hydrogen, aluminum, and small amounts of other ions. The aluminum content exceeded the hydrogen content in the original extracts for both clays, but the difference was greater for montmorillonite. In successive desaturations, the aluminum decreased until it tended to approach a constant value. Following this experiment, Chatterjee et al. (6) conducted a similar study on pure clay minerals bentonite, kaolinite, and pyrophyllite. The results were similar in most respects to those of the previous experiments, however, only in the case of kaolinite did the aluminum content exceed the hydrogen content in the first extracts. The decrease in displaceable acidity in succeeding desaturations was greater in bentonite than in the other minerals. The large decrease in displaceable acidity was apparently due to decomposition of bentonite because the cation exchange capacity also decreased and large amounts of SiO_2 were present in the extract. The indications were that pyrophyllite and bentonite were slightly affected by decomposition and that kaolinite was practically unaffected. Coleman et al. (8) noted that neutral salt leaching displaces both hydrogen and aluminum ions. It was further concluded that electrostatically bonded hydrogen ordinarily does not exist in important amounts in soils

and that exchangeable hydrogen as measured by buffer solutions is actually the sum of exchangeable aluminum and whatever weakly acidic groups that are ionized in the course of the determination. Coleman et al. (8) divided the soil charge into two components. The components were called permanent charge and a pH dependent charge. The two separate charges were defined as follows: (1) Permanent charges = all metallic cations in KCl extracts, and (2) pH dependent charge = the exchangeable acidity extracted by a BaCl_2 - Tri-ethanolamine solution following the neutral salt extraction.

It was found that the more strongly weathered soils tended to have smaller ratios of permanent charge/pH dependent charge than the less strongly weathered soils. This was probably due to a higher content of interlayer aluminum in the strongly weathered as compared to the less weathered soils. The permanent charge was countered almost exclusively by metallic cations and only negligible amounts of electrostatically bonded hydrogen was present in any of the soils studied. In soils having a pH below 6, aluminum was an important cation in neutralizing the permanent charge.

Heddleson et al. (17) found that exchange acidity consists of both aluminum and hydrogen. The strongly weathered, highly acid soils contained more aluminum on their exchangeable complex than less strongly weathered, less highly acidic soils. However, the less strongly weathered soils released more aluminum when they were acidified and extracted than did the strongly weathered soils when treated similarly. This is probably due to the fact that when the less weathered soils were treated with AlCl_3 more exchangeable aluminum could get in to the exchange sites. This is not the case with the highly weathered, highly acid soils simply

because they contain more aluminum interlayers which block or occupy exchange sites whereas in the less weathered soils these aluminum groups are fewer in number and only interfere minutely with aluminum exchange. The highly weathered soils containing more aluminum in extractable form is not easily explained by the observations above. It is then speculative that the acidification and extraction probably created the K_{sp} of free gibbsite around the edges of the clay layers, thus causing release, dissolution and crystallization of gibbsite which was determined in the extracts as exchangeable aluminum.

This is apparently not the case in the less highly weathered soils, because the aluminum interlayer groups do not appear in large quantities. Considerably less aluminum can be extracted from topsoils high in organic matter than from topsoils low in organic matter. Low (29) conducted a potentiometric and conductimetric titration study of electro-dialyzed bentonite, acid washed bentonite, and bentonite with various degrees of aluminum-hydrogen as determined by displacement with silver. He discovered that the titration curves of these clays had two inflection points, the first due to hydrogen and the second due to aluminum. It was concluded that hydrogen displaces aluminum in the layers, thus allowing exchangeable aluminum to increase at the expense of exchangeable hydrogen. Goates and Anderson (12) also found evidence for two types of acidic sites on clay minerals. No definite statements were made concerning the nature of these sites but it was noted by Harward and Coleman (14) that these sites could represent hydrogen and aluminum sites. Schwertman and Jackson (43), in a study utilizing a potentiometric titration procedure for acid saturated montmorillonite found a third acid site. This site was attributed to the basic aluminum

compounds formed in the presence of negative charges of montmorillonite.

Sawhney and Frink (42) obtained results similar to those of (43) except that the third acidic site was interpreted as being due to a complex alumino-silicate liberated from the clay by acid decomposition. This conclusion was based in part on the fact that the amounts of titrant required for the third acidic component increased both with aging and strength of the acid treatment.

The nature of the aluminum ions on the exchange complex may apparently be quite variable. The first aspect of this variability considered was the effect of pH on the type of acidic components. Schofield (44) found that clays develop additional negative charges above pH 6, but develop essentially no negative charges between pH 2.5-5. He also observed that acid washed clays exhibited buffering below pH 6, when titrated with alkali, but the buffering was attributed to the precipitation of exchangeable aluminum as aluminum hydroxide. Schofield stated that the aluminum ions must have been liberated during acid washing and retained as exchangeable ions. Pratt (34) found that the pH dependent cation exchange capacity between pH 3 and pH 8 was equivalent to the exchange acidity not displaced by neutral salts. The displacement was due to the presence of buffered BaCl_2 -tri-ethanolamine solution. Apparently, at least two acidic components were present and one was displaceable only at a higher pH. Hsu and Rich (20) reported that the only exchangeable ion is the Al^{3+} ion, and that in the correct acid range non exchangeable aluminum becomes fixed. Bhumbia et al. (3) found that the addition of lime to soils decreased both the exchangeable and pH dependent acidity. It was also reported that the pH dependent acidity measured by tri-ethanolamine extraction following KCL leaching decreased

markedly with the rate of liming.

Clay mineral properties affect the acidic properties of soils. Coleman et al. (7) studied acidity of bentonite-sesquioxide mixtures which had been artificially prepared by adding to separate clay samples Al_2Cl_3 along with either an equivalent amount of NaOH or $2/3$ of an equivalent amount. After completing the preparation, all samples were washed with Al_2Cl_3 solutions. The aluminum was determined, and as would be expected, the exchangeable aluminum levels were higher for the samples which had received a high level of aluminum in the sesquioxide additions than in the samples which had received a low level of aluminum. The hydrogen, (titratable but nonexchangeable acidity), was appreciable for all samples, but it was highest for those where the least aluminum was displaced. Similar, but less pronounced, effects were observed on samples which had received additions of iron. Considerable evidence has been accumulated in favor of the concept of soil acidity as an aluminum-hydrogen system. These new concepts have resulted in the explanation of old problems such as aluminum toxicity, estimating lime requirements, and pedochemical weathering. For a number of years it was not understood why old leached soils were not as acid as they would be expected to be if hydrogen clays were the ultimate product of soil weathering. The new concept is that the so-called hydrogen clays are products of weathering which formed during leaching and decomposed to mixed $H-Al(OH)_x^{3-x}$ clays. The aluminum ions then polymerize to form chemically inert interlayer sheets which reduce the exchange capacity and thus preserve the clay from further decomposition.

Why are aluminum clays acid and what are the exchange characteristics of aluminum? The mechanism by which aluminum is exchanged is

still not clearly understood. However, recognizing the replacement of clay layer cations by hydroxy-aluminum polymers and recalling the old observation that aluminum exchanged by KCL often exceeds titratable acidity, requires modification of some earlier views. First, clay layer replacement will remove exchangeable hydrogen and increase the number of aluminum ions on the clay surface. Second, to maintain low pH values, viz., having sorbed ions on the clay, and to account for replacement of some ions by dilute KCL and H-resin, the process of polymerization may be considered. The resulting surface may then be depicted as follows: There are four aluminum ions on the exchange complex instead of three, and the hydrogen ions tend to remain stationary because they cannot readily migrate to the crystal edges to release internal aluminum. Presumably, absorbed hydrogen ions move by exchange-diffusion switching positions with other surface cations (bulky aluminum-hydroxy-ions) which may become a rate limiting step that retards the breakdown of clays at the edge. The layer of aluminum-hydroxy-ions are very difficult to replace by dilute KCL and H-resins because these polymers cannot penetrate into the fine resin pores. But concentrated KCL should break up some of the polymers because of "anion penetration", Cl-replacing hydroxyl and aluminum hydroxyls becoming exchangeable. The aluminum ions do not appear to enter a hydrogen clay by exchange, and its behavior is different from that of the ferrous or lanthanum ion. In addition to studies made on the reaction of aluminum and its removal on saturated clays, there has also been some work performed on unsaturated clays.

Brown (5) found that the reaction proceeded so quickly that pH measurements made at various times from the start of the reaction gave no significant differences. He used this fact as an argument against

the theory that aluminum ions appear by a secondary process in solution. It has been pointed out that there is no conclusive proof that aluminum is directly exchanged but considering all facts involved, the exchange is of great importance.

Artificial Preparation of Hydroxy-Aluminum Interlayers. Aluminum interlayers in soil clays were observed to occur easily in the presence of a stable dioctahedral vermiculite by Brown (4). This observation has caused others to become curious as to the mechanism by which these naturally occurring aluminum groups form in the weathering process.

Reports of artificial preparation of aluminum interlayers in vermiculite were reported by Sawhney (40), and Rich (36). The choice of vermiculite was made apparently due to its high surface charge and great affinity for positively charged ions. This is probably due to the fact that most of the isomorphous substitution that occur in vermiculite is in the tetrahedral layer and since this layer is closer to the clay surface, vermiculite has a strong surface charge. Another factor to consider is that the vermiculite mineral is characteristically spaced at $14\overset{\circ}{\text{A}}$ which is intermediate in "c" spacing of the hydroxy-aluminum polymers occurring at pH 5 in an Al salt solution upon addition of alkali. Sawhney (41) showed that the treatment of clays from the lower soil horizons with hydroxy-aluminum saturations showed a greater affinity for polymer fixation as compared to those of the upper horizons. The effect is not as great in all clay types, which may be the results of poor crystallinity and a lower number of available exchange sites. This could result in slow diffusion of bulky hydroxy-aluminum polymers into interlayer positions which would partially compensate for the variation in fixation of the different horizons. Rich (36) discovered that the

presence of aluminum interlayers in soil clays reduces ammonium fixation to a great extent, and that treatment of soil clays with OH/Al solutions produces similar results. He also showed that clays that previously contained no interlayers refused to collapse to 10\AA , after treatment with hydroxy-aluminum solutions, upon potassium saturation and heating to 100°C .

Reports concerning the change in cation exchange capacity of clays after hydroxy-aluminum treatment have been given by (36, 43) and many others. Among the most classical reports was that of Rich (36) who reported a decrease in CEC from 134 to 1 meq/100g in a hydroxy-aluminum interlayered vermiculite.

Hsu and Bates (19) reported that the addition of vermiculite to hydroxy-aluminum solutions containing Al_2Cl_3 and NaOH resulted in fixation of hydroxy-aluminum polymers by the clay at much faster rates when the NaOH/Al ratio was in the range (0.3) to (2.1). The polymers produced from solutions in this range are of nearly constant composition and are very close to the formula $\left[\text{Al}_{10} (\text{OH})_{22} \right]^{8+}$ (double ring). These polymers are believed to be present in the interlayer spaces as single layers. By increasing the molar ratio from (2.25) to (2.70), the polymers held by clays gradually increase in size and decrease in net positive charge per aluminum atom. Increase in the molar ratios to (3.00) resulted in failure of the clay to fix aluminum interlayers. As a result crystalline $\text{Al}(\text{OH})_3$ formed outside the clay layers within a two week aging time. No crystalline gibbsite occurred in the specimens treated with OH/Al (2.7) even though samples had been aged for six months. Clay mineral particles are usually negatively charged and may be considered as large anions. From this point of view, clays with

hydroxy-aluminum polymers may be regarded as basic salts and may be expected to vary in stability. Barnhisel and Rich (1) reported that interlayer aluminum polymers in montmorillonite, prepared by treating clay with hydroxy-aluminum solution of NaOH/Al of (2.55) were not stable and were converted to gibbsite after prolonged aging. This suggested that the ability of gibbsite to form probably depends on how tightly the polymers are held in the interlayer spaces of montmorillonitic and kaolinitic clay minerals. Hsu and Bates (19) reported that when extra sodium hydroxide was added to a solution of NaOH/Al (2.7) to increase the molar ratio, the aluminum was completely removed from the solution after aging for two weeks, but the CEC of this specimen was similar to the untreated sample. X-ray diffraction patterns showed that the specimen collapsed to $10\overset{\circ}{\text{A}}$ upon K-saturation and the formation of crystalline $\text{Al}(\text{OH})_3$ was detected by DTA. This suggests that aluminum precipitated as $\text{Al}(\text{OH})_3$ outside the clay interlayer space and did not mechanically block the exchange reaction sites. Samples treated with hydroxy-aluminum solutions in the range of NaOH/Al (0.3) to (1.2) reduced the pH of the original solution. This change in pH, however, was completed within the first two weeks and then remained constant. The pH of solutions with ratios above (2.1) in the presence of vermiculite were slightly higher than that of the original solution. The increase in pH was probably due to partial breakdown of the larger hydroxy-aluminum polymers into smaller units.

Rate of Fixation. In discussing the rate of fixation both the amount of aluminum fixed and the time required to reach equilibrium should be considered. Shen and Rich (45) showed that in hydroxy-aluminum solutions of NaOH/Al (0.3) to (2.7), aluminum fixation

increased with an increasing ratio. Hsu and Bates (19) observed that the process of fixation for the above molar ratios reached equilibrium in two weeks. This was indicated by a constant concentration of aluminum in solution. A sudden break in the rate of fixation between ratios of (2.1) and (2.25) was observed, i.e., less aluminum was removed from solution. The process of fixation continues either until all of the aluminum is removed from solutions or possibly until the cation exchange positions are completely filled.

Polymer Size and Population. The hydroxy-aluminum polymers in a solution of NaOH/Al (2.1) and below are believed to be in the form of single ring units of composition, $\left[\text{Al}_6 (\text{OH})_{12} \right]^{6+}$ or double ring units $\left[\text{Al}_{10} (\text{OH})_{22} \right]^{8+}$. Sawhney (40) reported that these polymers are of the structure $\text{Al}(\text{OH})_2^+$ which are most abundant at pH 5. These polymers are relatively small, approximately 10 to $14\overset{\circ}{\text{A}}$ in diameter and $5\overset{\circ}{\text{A}}$ in thickness and will fit the interlayer space.

At molar ratios of (2.75) and above the polymers gradually increased in size with increasing NaOH/Al. The development in the "a" and "b" directions occur and possibly build in the "c" direction into two or more layers. If this is the case, then these large polymers would have to be sheared into one layer before they could enter the interlayer space of vermiculite. This might explain why the sudden break in the rate of fixation occurs in high molar ratios. When clay interlayer spaces become somewhat crowded, the entrance of other units may be retarded physically due to lack of space between clay layers or chemically as a result of unfavorable charge distribution. Consequently any further fixation of hydroxy-aluminum polymers must be accompanied by a redistribution of the earlier occupants. The more tightly the

clay holds hydroxy-aluminum polymers the more slowly the polymers already present in the clay interlayer space redistribute themselves. When vermiculite was treated with an OH/Al of (0.6), Hsu and Bates (19) noticed an equilibrium of fixation was reached within two weeks of aging. Another sample of the same size was treated with an increased volume of NaOH/Al (0.6) and equilibrium did not occur in two weeks. This is probably due to the fact that the number of polymers present in the first solution were so low that all of them could easily enter the clay. This was not the case with the increased volume of the same value because a greater number of polymers were provided which could not be as readily taken up by the clay as in the smaller volume solution. It is believed that the higher the molar ratio of these solutions the greater the polymers are in numbers and in size.

Sawhney (40) has shown that an increase in cation exchange capacity is a measure of the stability of Al-interlayers, but found little or no correlation between the change in cation exchange capacity and the amounts of aluminum extracted by Na-citrate. Soil clay interlayers are generally assumed to be composed largely of aluminum, but there have been reports of nearly pure iron interlayers on one soil by Deshpande et al. (9). They reported that iron oxides are not important as cements in clay particles. The properties of the precipitate that is formed upon addition of an alkali hydroxide solution to a solution of aluminum salt has been the subject of much discussion. MacKenzie (30) has indicated that the freshly formed gelatinous precipitate from aluminum chloride or nitrate exhibits the structure of boehmite (α Al(OH)₃) and upon aging the boehmite structure changes into bayerite (β Al(OH)₃) and finally into gibbsite (γ Al(OH)₃). Barnhise1 and Rich (1) showed

that the amount of gibbsite formed in clay samples after one month of aging when treated with OH/Al solutions of (2.55) and (3.00) increased with time. The interlayers formed in these samples were not stable and x-ray diffraction patterns showed complete closure of the interlayer space from 14 to 10 $\overset{\circ}{\text{A}}$. This was attributed to the poor holding capacity of the clay which allowed hydroxy-aluminum polymers to migrate from within the interlayer spaces and precipitate as gibbsite in the aging solution. It was also reported that it is significant that gibbsite forms in montmorillonite systems under acid conditions. This is in contrast to a neutral to alkaline pH apparently required for gibbsite formation in a pure or clay free system. Gibbsite has been found in many acid soils of the Piedmont and Coastal Plain regions. In many of these soils, gibbsite was only a minor part of the clay fraction (< 1%); however, in some soils gibbsite amounted to over 40% of the clay fraction. It is then plausible that the gibbsite in some of these acid soils may have formed with an intermediate step involving aluminum interlayers. This suggests that gibbsite formation may be active particularly if the soils are not limed. The possibility of Al(OH)₃ being absorbed on the clay surface and that its solubility is related to this sorption is suggested by Ragland and Coleman (35) and discussed by Jackson (22). Barnhisel and Rich (1) reported that considerable time is needed for gibbsite to form and that the time required may be affected by the presence of clay so that the magnitude of Al(OH)₃ would be a function of time. Ragland and Coleman (35) reported that some montmorillonite and kaolinite samples revealed some precipitation of Al(OH)₃ between their interlayer spaces and prevented the collapse of these minerals on heating. Samples that contained 440 and 880 meq. Al(OH)₃ per 100 g. clay

retained their interlayer hydroxide, whereas the samples with 1100meq. lost their interlayer hydroxide and collapsed on K-saturation and heating to 100° C. It was also shown that as much as 0.2 mmol. of aluminum was removed from a solution of $10^{-3} M Al_2Cl_3$ by 1-gram of montmorillonite and kaolinite over a two day period.

CHAPTER III

LABORATORY METHODS AND PROCEDURES

Fifty gram samples of Hartsell and Choteau soils were fractionated and the $2-0.2\mu$ and $<0.2\mu$ size fractions were prepared for x-ray diffraction analysis according to a procedure described by Jackson (23). Interlayer material was extracted with 100ml portions of 1M sodium citrate from approximately 1.0 gram samples heated in a water bath at $80-90^{\circ}$ C. The citrate solution was renewed hourly and samples were removed after 6 hours of extraction for CEC determination by calcium saturation and sodium replacement.

Hydroxy-aluminum polymers were introduced into clay interlayer positions by the dropwise addition of 0.1M NaOH and $0.2M Al_2(SO_4)_3 \cdot 18H_2O$ to the clay fractions in suspension form. Clay suspensions were kept in a mobile state by the use of a magnetic stirrer while salt and base were added. The amount of aluminum left in solution at the end of each aging period was determined by the method of Hsu (18). Samples were allowed to age for a period of six months and then washed free of excess aluminum and sodium with deionized water. Surface area of all clay fractions was obtained by the use of a recent method of Jacobs and Morin (25). Potassium oxide content of illite was determined on each clay fraction by digesting 0.1 gram samples with HF.

After digestion, samples were brought to a 100 ml volume with 5 ml of 0.5N HCL and 95 ml of deionized water. The amount of potassium in

the extracts was measured by atomic absorption spectrophotometry. Aluminum in the amorphous material and interlayer spaces was determined by rapid dissolution of clay samples by the method of Hashimoto and Jackson (15).

CHAPTER IV

RESULTS AND DISCUSSION

The addition of hydroxy-aluminum solutions of variable NaOH/Al to Hartsells and Choteau clay fractions resulted in aluminum polymer fixation. Coarse clay (2-0.2 μ) fractions of both soils fixed more aluminum polymers than fine clay (< 0.2 μ). The reason for a greater polymer fixation in coarse clay than in fine clay has not been fully explained. The fine clays of these soils have high CEC and low K₂O contents. Coarse clays show a higher K₂O content and lower CEC. These values given in Table I suggest a mixed clay mineralogy with 10-20% illite. Since the fine clays appear to be largely montmorillonitic, it can be concluded that hydroxy-aluminum polymers were not held tightly enough in the interlayer space for substantial fixation. As a result, these polymers migrated to the clay crystal edges and back into solution. Hydroxy-aluminum polymers are not held in the interlayer spaces of montmorillonite as tightly as vermiculite or beidellite due to a lower surface charge and weak bonding in the octahedral-tetrahedral coordination.

X-ray diffraction patterns (Figure 1) show that the crystallinity of the fine clay is not as pronounced as the coarse clay as shown in Figure 2. Rapid dissolution of these clays by the method of Hashimoto and Jackson (15) further clarifies the poor crystalline structure exhibited by the fine clay fractions. Table II shows that as much as 20% Al₂O₃ was extracted from fine clay while only 9% Al₂O₃ was extracted

TABLE I
SURFACE AREA AND ILLITE CONTENT OF CLAYS STUDIED

Sample	Specific Surface m ² /g. clay		% K ₂ O	% Hydrous Mica* (illite)
	Total	External		
Choteau (< 0.2μ)	479	373	1.36	13.6
(2-0.2μ)	310	179	1.16	11.6
Hartells (< 0.2μ)	602	346	2.38	19.2
(2-0.2μ)	240	139	1.92	19.2

*Percent mica was obtained by assuming that 10% of the soil clay mica mineral was 10% K₂O by weight.

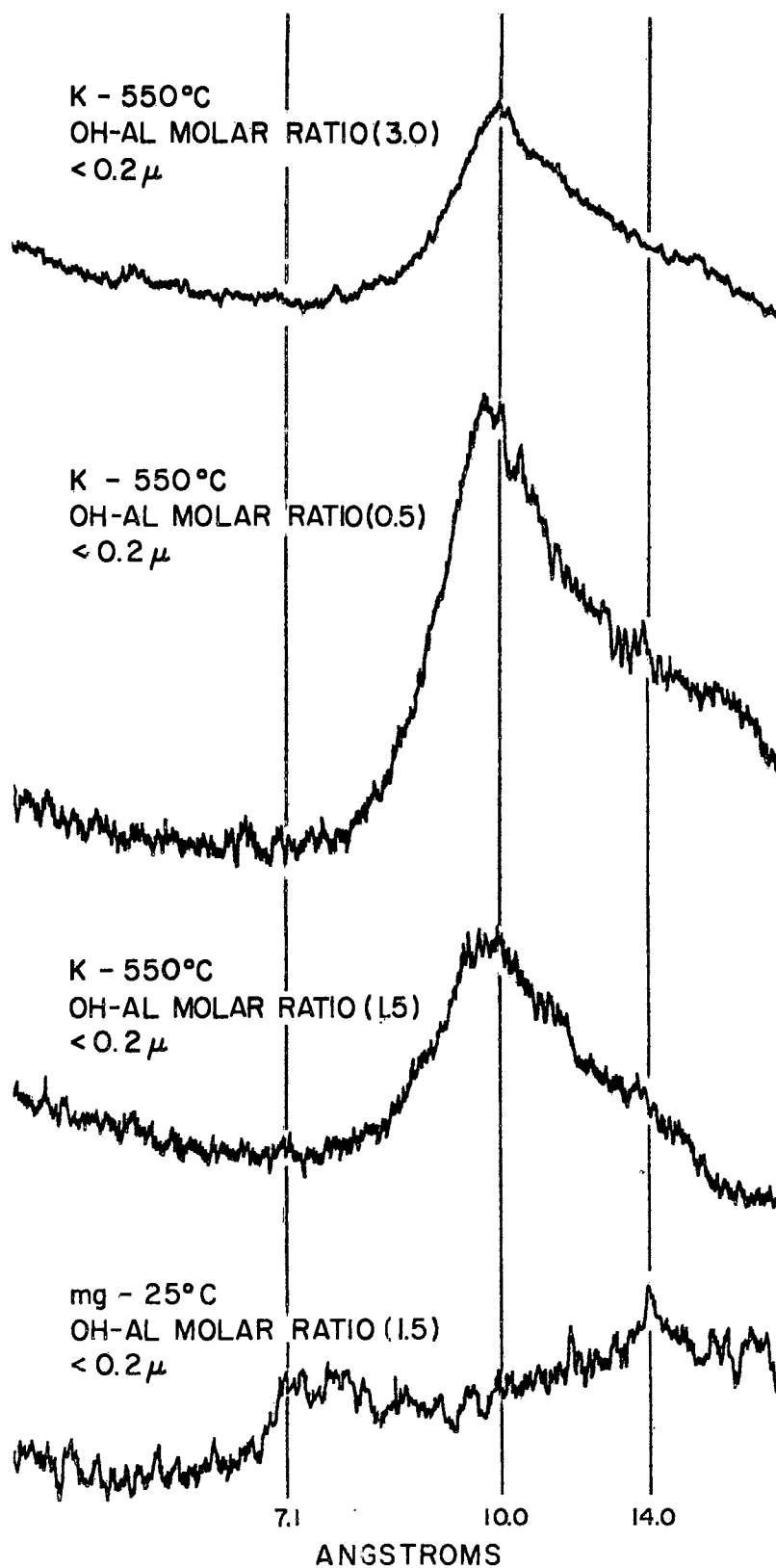


Figure 1. X-ray Diffractograms of Choteau Fine Clay (<math>< 0.2 \mu</math>)

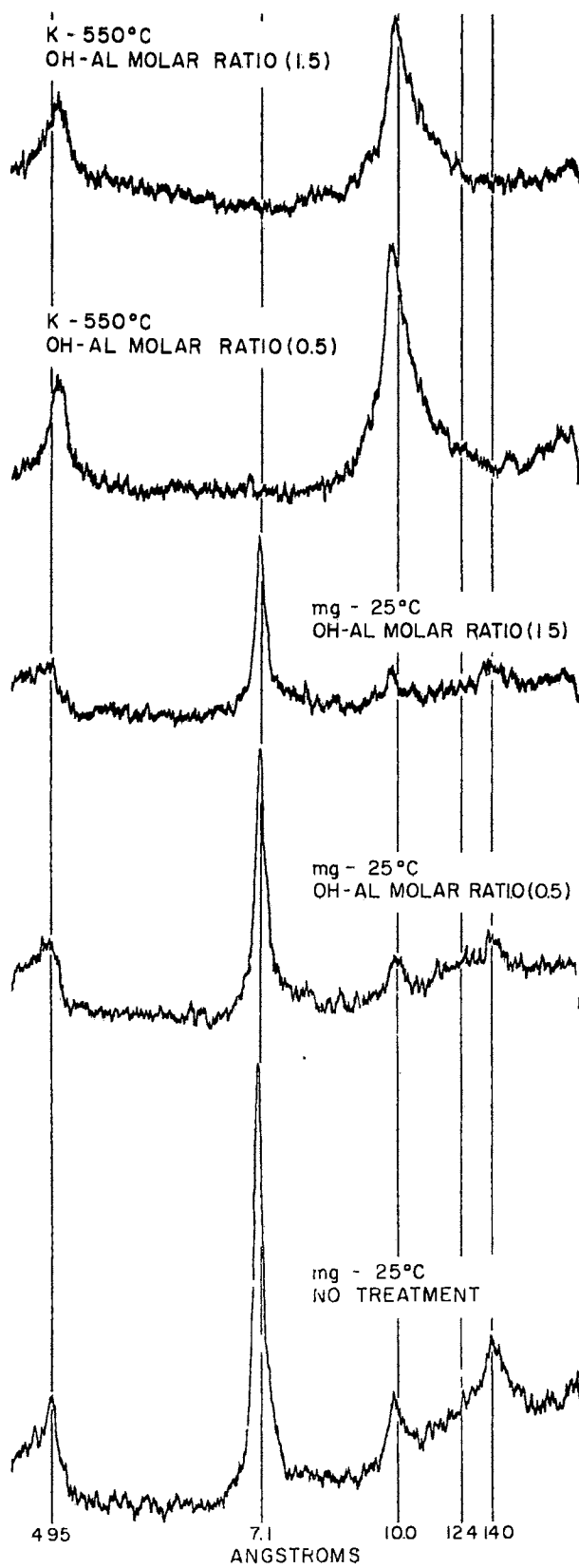


Figure 2. X-ray Diffractograms of Hartsell's Coarse Clay (2-0.2 μ)

TABLE II
 DISSOLUTION ANALYSIS OF CLAYS FOR AMORPHOROUS CONSTITUENTS
 AND INTERLAYER ALUMINUM

Sample	Amorphorus	Interlayer	Amorphorus (check)*
%Al ₂ O ₃			
Choteau (< 0.2μ)	19.2	32.4	19.6
Hartsells (< 0.2μ)	20.3	27.6	20.9
Choteau (2-0.2μ)	9.2	15.1	8.5
Hartsells (2-0.2μ)	7.6	17.7	7.3

*Analysis made to determine if samples were free of precipitated gibbsite.

from coarse clays using the procedure designed to only extract amorphous aluminum. The amount of Al_2O_3 was very high as compared to 1-2% usually exhibited by crystalline clay minerals. These data indicate that the fine and coarse clays are both poorly crystalline with the poor crystallinity in the fine clay fraction. X-ray diffraction patterns show that these clays are aluminosilicates and are not completely amorphous. When these clays were K-saturated and heated to $550^{\circ}C$, they collapsed to 10\AA . This type of response is typical of layer aluminosilicates.

It is surmised that a considerable quantity of the fine clay fractions of these soils is amorphous, but a haphazardly arranged crystalline structure still exists. Clays of these characteristics are not expected to fix hydroxy-aluminum polymers to any great extent because of their weak configuration, poor bonding strength between crystal layers and random distribution of exchange sites. Chemical data (Table I) indicate that the type of clay in these two soils are similar and as a result, the variation in aluminum polymer fixation was small. There were small indications of a greater fixation of occurring aluminum in Choteau than in Hartsell's coarse clay.

Variation in Cation Exchange Capacity. Treatment of Hartsell and Choteau clay fractions with hydroxy-aluminum solutions produced reductions in cation exchange capacity. These changes can be observed in Table III which shows that the exchange capacities of the coarse clays were reduced considerably more than fine clays. These changes in cation exchange capacity correlate very well with the sorption data as shown in Tables IV and V. It may be observed that the coarse clay sample sorbed more hydroxy-aluminum polymers and as a result suffered a greater loss in cation exchange. Little or no change in CEC was observed in

TABLE III
 VARIATIONS IN CATION EXCHANGE CAPACITY
 DUE TO ALUMINUM TREATMENT

NaOH/A1	Meq./100g. clay			
	Choteau*		Hartsell†	
	2-.2 μ	<0.2 μ	2-.2 μ	<0.2 μ
0.00	42.1	86.1	35.7	62.3
0.50	8.2	82.7	13.0	57.7
1.00	8.0	88.5	11.5	55.2
1.50	5.3	82.8	7.4	57.1
2.00	9.1	82.7	19.3	53.7
2.50	14.1	79.3	29.1	50.3
2.75	43.4	83.7	37.2	62.8
3.00	45.3	88.8	43.1	68.9

Original CEC:

* Choteau (2-.2 μ) = 52.1meq./100g. clay

" " " " (<0.2 μ) = 92.4 " " " " " " " "

+ Hartsell (2-.2 μ) = 47.9 " " " " " " " "

" " " " (<0.2 μ) = 67.0 " " " " " " " "

TABLE IV
 CHANGES IN CONCENTRATION OF ALUMINUM IN SOLUTION
 DURING AGING OF ORIGINAL CLAYS

NaOH/A1	Concentration of A1 in solution* (150ml solution/gram clay)		
	μg A1/ml		
<u>CHOTEAU COARSE CLAY (2-0.2μ)</u>			
	<u>1-week</u>	<u>6-weeks</u>	<u>6-months</u>
0.00	418.3	402.1	401.2
0.50	325.0	312.3	310.2
1.00	318.7	309.6	308.6
1.50	306.3	294.3	293.8
2.00	256.3	214.2	240.6
2.50	193.7	186.3	185.3
2.75	325.0	319.3	318.8
3.00	318.7	306.4	305.9
<u>HARTSELL COARSE CLAY (2-0.2μ)</u>			
0.00	486.2	443.2	442.5
0.50	350.0	327.6	326.1
1.00	318.7	303.1	303.0
1.50	304.7	293.6	292.3
2.00	259.4	243.4	241.9
2.50	196.9	190.2	188.2
2.75	331.3	322.3	320.6
3.00	324.8	320.4	318.3

*Original concentration of aluminum solution = 540μg/ml

TABLE V
 CHANGES IN CONCENTRATION OF ALUMINUM IN SOLUTION
 DURING AGING OF ORIGINAL CLAYS

NaOH/A1	Concentration of A1 in solution [*] (150ml solution/gram clay)		
	$\mu\text{g A1/ml}$		
<u>CHOTEAU FINE CLAY (< 0.2μ)</u>			
	<u>2-weeks</u>	<u>6-weeks</u>	<u>6-months</u>
0.00	499.4	468.2	467.2
0.50	456.3	461.3	460.1
1.00	456.3	445.3	443.2
1.50	431.3	433.3	429.3
2.00	422.4	422.1	421.3
2.50	410.3	409.2	408.9
2.75	421.1	480.6	515.2
3.00	515.2	514.2	512.8
<u>HARTSELLS FINE CLAY (< 0.2μ)</u>			
0.00	485.8	440.0	439.3
0.50	465.6	427.5	426.2
1.00	443.7	413.3	413.3
1.50	428.1	401.9	402.3
2.00	421.3	389.2	390.2
2.50	396.8	364.8	363.5
2.75	475.0	448.6	449.0
3.00	525.0	510.4	511.1

*Original concentration of aluminum solution = 540 $\mu\text{g/ml}$

clays treated with solutions of NaOH/Al (0.00), (2.75), and (3.00). At NaOH/Al (0.00), there was very little polymer fixation due to the absence of free hydroxyls needed to form the aluminohexahydronium ion configuration. Results show that there were small amounts of aluminum lost from the reference solution. This loss is probably due to certain exchange reactions and error in the determination of aluminum. The small amount of polymer fixation that occurred with solutions of NaOH/Al (2.75) and (3.00) was probably due to the formation of polymers too large to fit freely into the interlayer space. Reports by Hsu and Bates (18) postulated that the hydroxy-aluminum polymers formed in a solution of NaOH/Al above (2.50) exist as double ring units of composition $\left[\text{Al}_{10} (\text{OH})_{22} \right]$. Other polymers of smaller sizes formed in NaOH/Al solutions 2.75 probably entered the interlayer space freely and thus reduced the cation exchange capacity.

The fine clay of these soils exhibited entirely different characteristics. There was essentially no aluminum interlayer fixation. The data in Table VI shows that citrate treatment only caused small increases in CEC. The reason for this is that the fine clay fractions of these soils contain little or no initial aluminum interlayers. Therefore, citrate treatment did not affect the cation exchange capacity since all of the exchange complexes were already in a free state. The data given in Table IV also shows that the CEC of the fine clays were not affected by the aluminum treatment to any noticeable extent which indicates that little or no hydroxy-aluminum polymer fixation occurred. These types of results would indicate that the mechanisms responsible for aluminum interlayer fixation is not one merely of charge attraction. The other factors to be considered consist of crystallinity, mineral type,

TABLE VI
 CHANGES IN CEC OF CLAYS AFTER CITRATE EXTRACTION
 AND OH-ALUMINUM TREATMENT

Sample	NaOH/Al	Cation Exchange Capacity		
		Initial	Citrate extracted	OH-Al [*] treated
meq./100g. clay				
Choteau (< 0.2 μ)	0.5	92.4	105.3	103.6
" " " " " " " " " " " "	1.5	92.4	105.3	97.7
Hartells (< 0.2 μ)	0.5	67.4	79.2	66.9
" " " " " " " " " " " "	1.5	67.4	79.2	61.5
Choteau (2-0.2 μ)	0.5	52.1	89.5	22.3
" " " " " " " " " " " "	1.5	52.1	89.5	3.4
Hartells (2-0.2 μ)	0.5	47.9	74.2	18.5
" " " " " " " " " " " "	1.5	47.9	74.2	13.7

* 50ml of solution per 100mg. clay.

interlayer spacing between clay crystal layers and possibly clay particle size.

Pre-citrate extracted samples treated with hydroxy-aluminum solutions of molar ratios (0.5-1.5) produced the largest reduction in cation exchange in coarse clays and are shown in Table VI. These data indicate that the CEC of these soils are greatly influenced by the degree of interlayer deposition which is a function of the clay mineral type.

Largest reduction in cation exchange capacity was observed in Choteau coarse clay treated with solutions of NaOH/Al of (1.50). The extraction of interlayer aluminum from these clays with N Na-citrate increased their cation exchange capacity. The results shown in Table IV indicate that the largest increase occurred in the coarse clay fractions. From these data it was concluded that during the chemical weathering process, aluminum interlayers preferentially deposited in the coarse clay fraction of these soils rather than in the fine clay.

NaOH/Al treatment of pre-citrate extracted clays also suffered a loss in cation exchange capacity due to aluminum polymer fixation. The fixation of hydroxy-aluminum polymers in fine clay was less than in coarse clay. The coarse clays fixed aluminum polymers to such an extent that their cation exchange capacity was lowered below the initial value. This indicated that the artificially prepared hydroxy-aluminum polymers were able to migrate into the interlayer spaces of the coarse clay fractions more freely and cling to the negatively charged surfaces. This was made possible when these clays were extracted with citrate which removed the interlayer aluminum and freed the exchange sites. This extraction increased the ability of the clay particles to attract the positively charged hydroxy-aluminum groups which resulted in greater

polymer fixation within the clay interlayer spaces.

Rate of Hydroxy-Aluminum Polymer Fixation. A variation in hydroxy-aluminum polymer fixation rate was noticed in Hartsell and Choteau clay fractions. These variations were primarily a result of clay mineral type and the NaOH/Al employed. The data in Tables IV and V indicate that the largest portion of polymer fixation occurred within the first two weeks. A continuation of the aging period to 6 months produced no noticeable change in the amount of aluminum fixed. The sorption of hydroxy-aluminum polymers was more pronounced in coarse than in fine clay. The fine clays sorbed less aluminum from solution possibly due to their poor crystallinity. The rate of fixation occurring in pre-citrate extraction samples was considerably higher than samples that were not citrate extracted. Hydroxy-aluminum polymer fixation was essentially ended in the first two weeks of aging and no noticeable fixation occurred throughout the 6 month aging period.

Citrate extracted samples were able to fix more hydroxy-aluminum polymers because of the destruction of naturally occurring interlayer material. Polymers were able to migrate into the interlayer spaces freely and distribute themselves at will. The highest amount of aluminum fixation occurred using a NaOH/Al of (1.5) and is shown in Table VII. Hsu and Bates (19) reported that artificially prepared hydroxy-aluminum polymers increase in size with increasing NaOH/Al. They also reported that these polymers are relatively small and exist in sizes ranging from $10\overset{\circ}{\text{A}}$ to $14\overset{\circ}{\text{A}}$ in diameter and $5\overset{\circ}{\text{A}}$ in thickness. Considering these reports, it was concluded that hydroxy-aluminum polymers formed in a solution of NaOH/Al 1.5 was very close to $14\overset{\circ}{\text{A}}$ in diameter and $\pm 5\overset{\circ}{\text{A}}$ in thickness. It appears that the polymers formed in a solution of this

TABLE VII
 CHANGES IN CONCENTRATION OF ALUMINUM IN SOLUTION
 DURING AGING OF CITRATE EXTRACTED CLAYS

Sample	NaOH/A1	Concentration of A1 in solution 50ml solution/100mg. clay*		
		μg A1/ml		
		1-week	6-weeks	6-months
Choteau (2-0.2μ)	0.5	287.5	252.3	251.3
" " " " " " " " "	1.5	112.8	99.8	89.2
Hartells (< 0.2μ)	0.5	531.3	479.2	479.0
" " " " " " " " "	1.5	518.8	505.3	502.5
Choteau (< 0.2μ)	0.5	531.3	501.9	507.3
" " " " " " " " "	1.5	468.8	465.5	465.3
Hartells (2-0.2μ)	0.5	325.0	278.2	276.9
" " " " " " " " "	1.5	187.5	135.5	134.5

*Original concentration of aluminum solution = 540μg/ml

ratio were able to migrate into and attach themselves to the clay crystal sheets in greater quantities and at faster rates than the other size polymers.

X-Ray Diffraction Analysis. The coarse clay fraction of Choteau and Hartsells soils did not expand to 18\AA when Mg^{++} -saturated, and ethylene glycol solvated, but did partially collapse to 10\AA upon K^+ -saturation at room temperature. The degree of collapse was greater in Choteau coarse clay than Hartsells coarse clay which indicates that less interlayer aluminum was present. Heating these samples to 550°C . caused complete collapse to 10\AA . These results suggest a vermiculitic type clay with aluminum interlayers. Representative patterns of these clays are shown in Figures 3, 4, and 5. These figures also show that there is a difference in the amount of aluminum interlayers present in each clay. It should be noticed that Choteau coarse clay exhibited a sharper 10\AA peak than Hartsells coarse clay after 2 hours of citrate extraction. This would indicate that essentially all of the interlayer aluminum present in the Choteau coarse clay was removed by citrate extraction, however, there is still a considerable amount of interlayer material left in the Hartsells coarse clay which accounts for the broadness of the 10\AA peak as illustrated in Figures 3 and 4.

The fine clay of these soils appeared essentially amorphous to x-ray diffraction when they were Mg^{++} -saturated and ethylene glycol solvated at room temperature. This created difficulty in identification of the dominant mineral present and gave poor indications pertaining to aluminum interlayer content. Heating these samples to 550°C . resulted in collapse to 10\AA which is a diagnostic characteristic of layer alumino-silicates, and is shown in Figure 5. Following hydroxy-

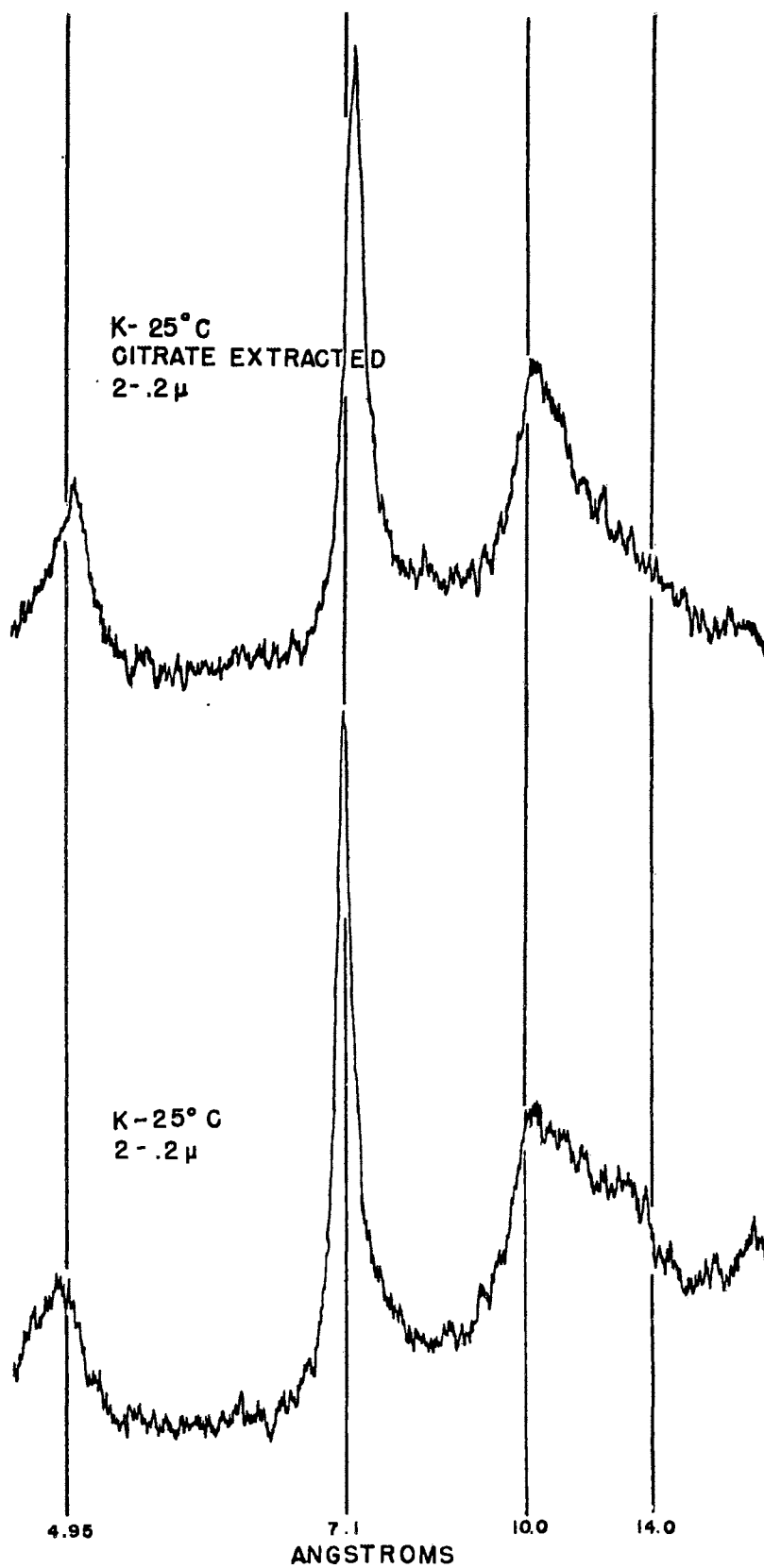


Figure 3. X-ray Diffractograms of Hartsell's Coarse Clay (2-0.2μ)

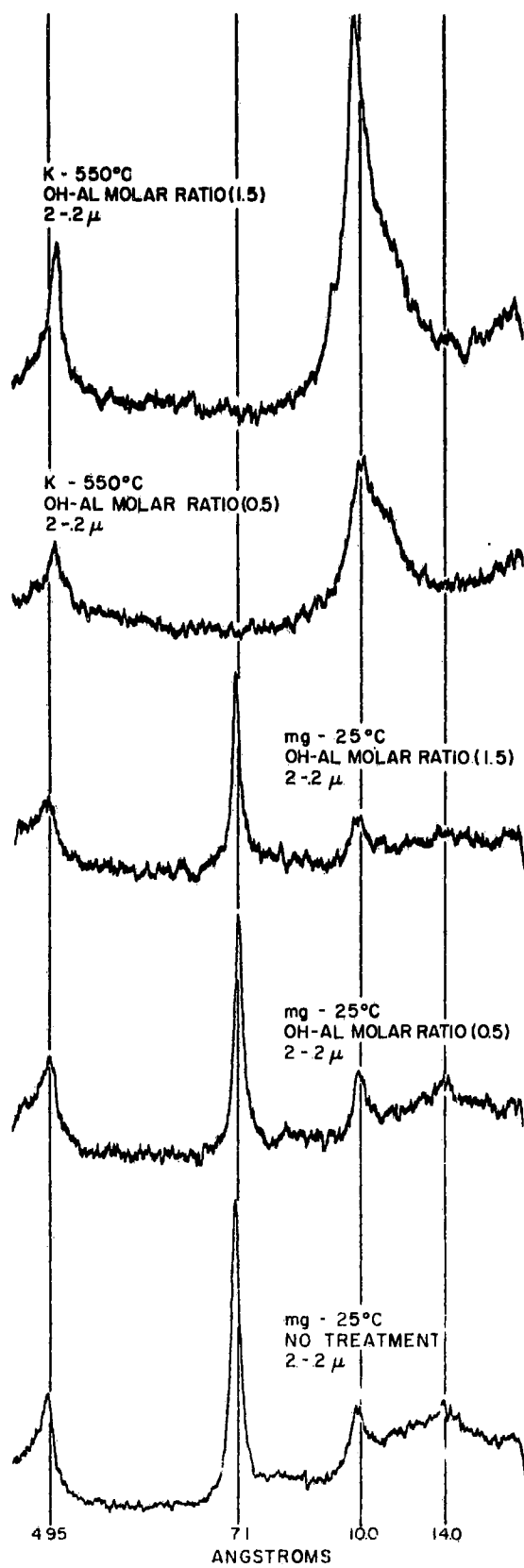


Figure 4. X-ray Diffractograms of Choteau Coarse Clay (2-0.2μ)

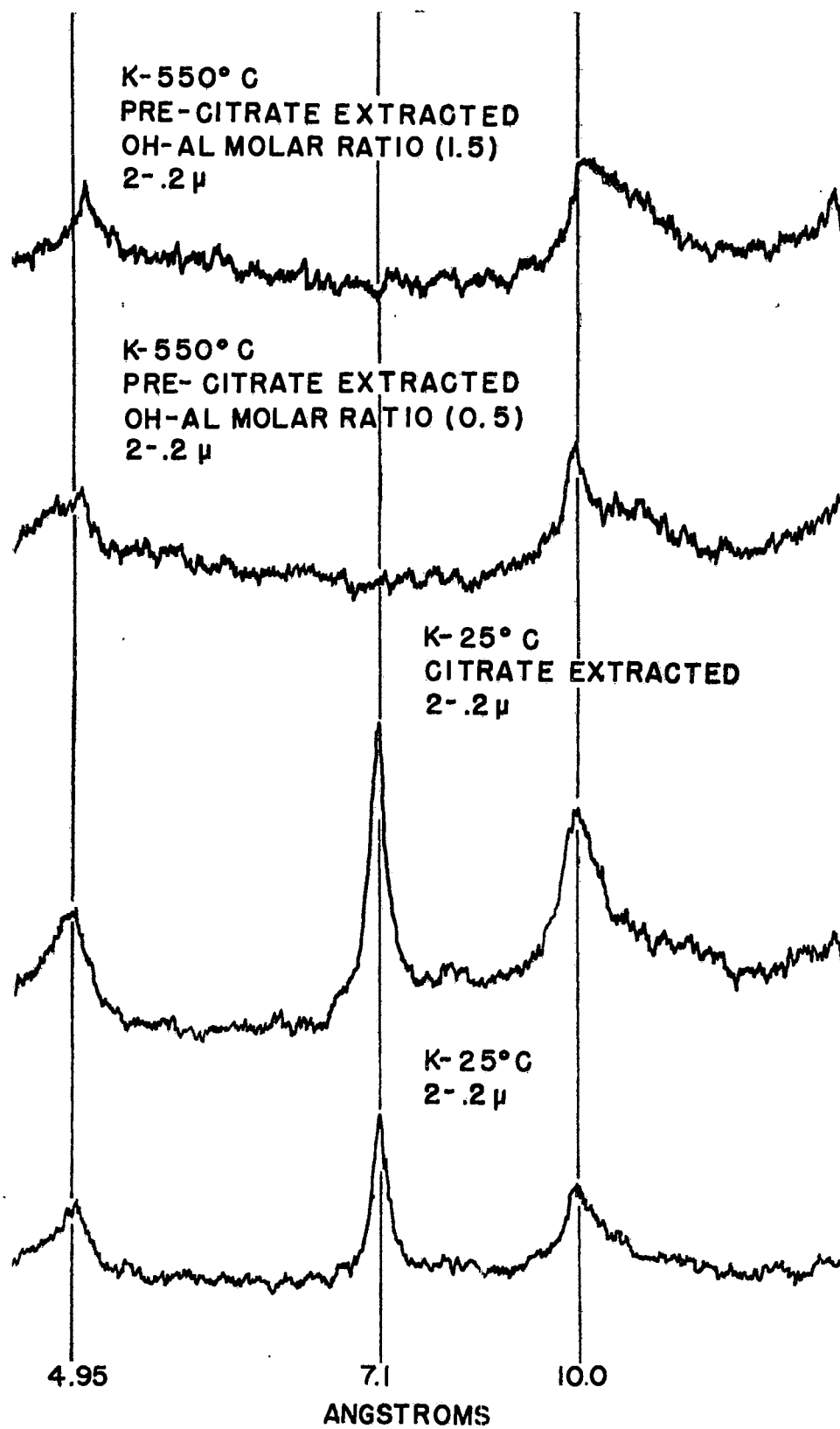


Figure 5. X-ray Diffractograms of Choteau Coarse Clay
(2-0.2μ)

aluminum treatment of citrated extracted Hartzell and Choteau coarse clay, a stable 14\AA peak was observed upon K^+ -saturation at room temperature. Figure 6 shows that the basal spacing of these clays approached 10\AA as the temperature was increased to 550°C . This would indicate that the hydroxy-aluminum polymers fixed in the interlayer spaces of these clays were very stable.

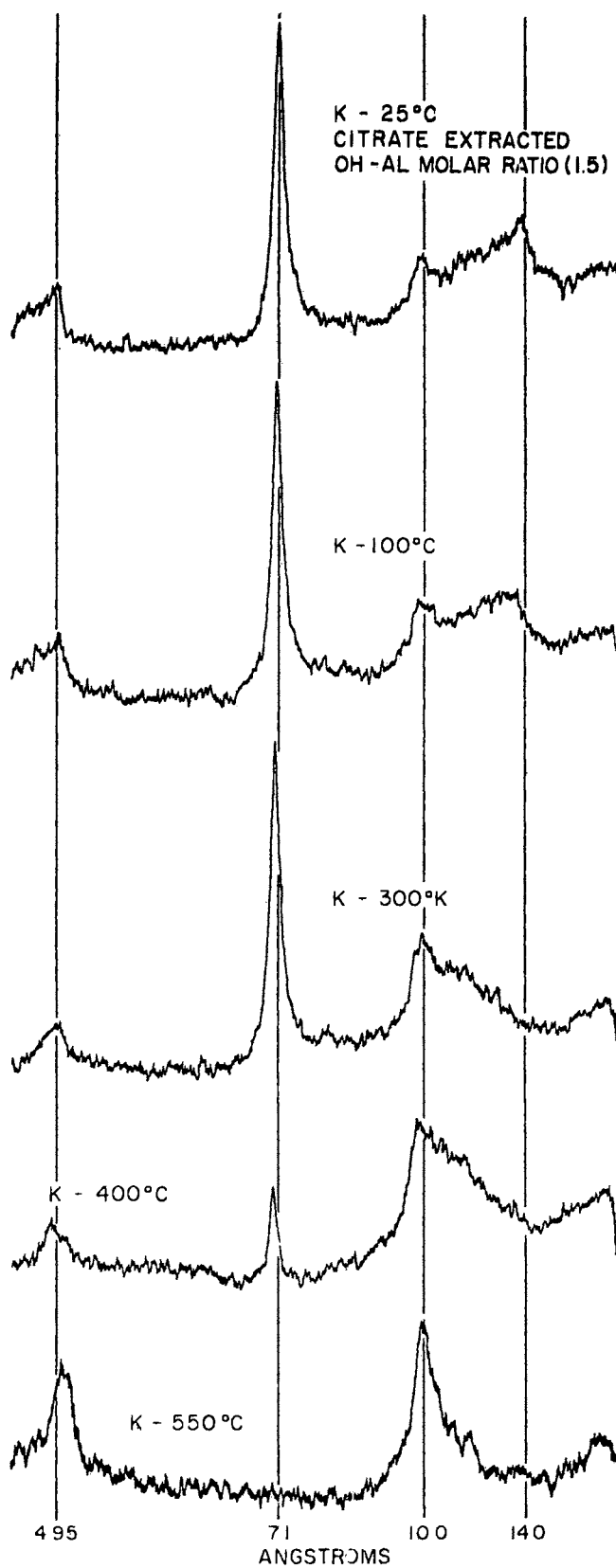


Figure 6. X-ray Diffractograms of Hartsell's Coarse Clay (2-0.2 μ)

CHAPTER V

SUMMARY AND CONCLUSION

The fixation of hydroxy-aluminum polymers varied among fine and coarse clay fractions of Hartsells and Choteau soils. Aluminum fixation was more pronounced in coarse clays than in fine clays and as a result the coarse clays showed the greatest loss in CEC. The sorption of hydroxy-aluminum polymers from solution was also higher among coarse clays than in fine clays. Choteau coarse clay fixed more hydroxy-aluminum polymers than Hartsells and was less resistant to interlayer extraction. It is concluded that Choteau coarse clay fixed more hydroxy-aluminum polymers than Hartsells coarse clay because of greater openings that existed within its interlayer spaces. The fine clay fraction of these soils did not fix hydroxy-aluminum polymers to any noticeable extent. This is believed to be a result of its poorly crystalline structure, and the existence of montmorillonite as the predominant clay mineral. The coarse clay fraction of both soils showed a loss in CEC when they were pre-citrate extracted and then aluminum treated. The fine clays showed only a small increase in CEC when they were treated in the same manner. These results would indicate that the magnitude of aluminum interlayer deposition is not one mainly of clay crystal charge, but includes other factors such as crystallinity and size of clay particles. A more pronounced hydroxy-aluminum polymer fixation occurred in pre-citrate extracted coarse clay samples due to an increase in available

exchange sites and the ability of these polymers to distribute themselves in the clay interlayer spaces. An occurrence of more aluminum interlayers in the original Hartsells coarse clay than in Choteau is probably due to a variation in parent material from which the two soils were derived.

The natural or artificial occurrence of aluminum interlayers in soils have many important effects on the properties of the clays present. The degree of effect depends upon the type of mineral present which will govern the magnitude of aluminum interlayer deposition.

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APPENDIX

Hartsells fine sandy loam

Location: Pittsburg County, Oklahoma. About 800 feet east and 350 feet south of the half mile line on the north side of Section 8, T5N, R13E.

Native Vegetation: Post oak, blackjack oak, and hickory trees with a tall grass understory. Used for rangeland.

Parent Material: Noncalcareous sandstone of Pennsylvanian Age.

Slope and Land Form: Slope is 2 percent on erosional upland.

A1 17144	0-3 ¹¹	Dark grayish brown (10YR 4/2) fine sandy loam, grayish brown (10YR 5/2) dry, weak fine granular structure; very friable, slightly hard, pH 5.5; clear boundary.
A 21	3-10 ¹¹	Grayish brown (10YR 5/2) fine sandy loam; light gray (10YR 7/2) dry, weak fine granular structure; very friable, slightly hard; pH 5.5; diffuse boundary.
A 22 17146	10-17 ¹¹	Pale brown (10 YR 6/3) fine sandy loam, light gray (10 YR 7/2) dry; weak fine granular structure; very friable, slightly hard; pH 5.5; clear boundary.
B21t 17147	17-27 ¹¹	Yellowish brown (10YR 5/6) light sandy clay loam; few grayish brown mottles; light yellowish brown (10YR 6/4) dry; moderate medium subangular blocky structure; friable, hard; sand grains on ped faces are coated with clay films; pH 6.0; diffuse boundary.
B22t 17148	27-36 ¹¹	Brownish yellow (10YR 6/6) sandy clay loam; common medium distinct yellowish red and grayish brown mottles; yellow (10YR 7/6) dry; moderate medium subangular blocky structure; friable, hard; sand grains on ped faces are coated with clay films; pH 5.0; gradual boundary.
B 3 17149	36-48 ¹¹	Brownish yellow (10YR 6/6) sandy clay loam; many medium distinct light gray mottles and common medium prominent strong brown mottles; yellow (10YR 7/6) dry; moderate medium subangular blocky structure; friable, hard; a few sandstone fragments are present; pH 5.0; clear wavy boundary.

R1 17150	48-66''	Highly weathered, loosely cemented, fine grained sandstone that has thin stratified and mottled layers of grayish brown to yellowish red sandstone; an average color of the horizon would be yellowish brown (10YR 5/6); an average texture would be sandy clay loam; massive structure; friable, hard; about 15 percent of the mass is sandstone fragments; pH 5.0.
R2 17151	66-80''	Same as the R1 horizon except color. This horizon is yellowish brown (10YR 5/8) mottled with light brownish gray (10YR 6/2).

Choteau silt loam - L

Location: Southeast of Muskogee on the Oklahoma State University Pasture station. 685 feet north and 280 feet east of the southeast corner of SE 1/4, of Section 32, T14N; R17E.

Native Vegetation: Tall grass prairie, but near the forest-grass tension zone. Prairie consisted of Big Bluestem (Andropogon gerardi), Little Bluestem (A. scoparius). Land is now in cultivation.

Parent Material: Weathered siltstone or silty shales.

Topography: Smooth 2-2.5% north facing footslope joining soils on steeper slopes.

Soil Profile:

Ap	0-10"	Dark grayish brown (10YR 3.0/2 moist) silt loam, grayish brown (10YR 5/2); weak fine granular; friable; permeable; numerous roots and worm casts; pH 5.6; grades to horizon below.
A21	10-18"	Dark grayish brown (10YR 4/2 moist) silt loam, grayish brown (10YR 5/2); porous massive, very friable and hard; permeable; numerous roots and many worm casts; few faint stains of dark yellowish brown (10YR 4/4); pH 5.0; clear boundary.
A22cn	18-24"	Brown (10YR 5/3 moist) silt loam, light brownish gray (10YR 6/2); very porous massive; very friable and very hard; clear distinct stains or mottles of dark yellowish brown (10YR 4/4), much of the color due to fine and medium ferruginous concretions; small pockets of soil material from the AP; many worm casts; pH 5.0; clear boundary.
B1	24-30"	Brown (10YR 5/3 moist) heavy silt loam, pale brown (10YR 6/3); very weak, medium blocky to somewhat porous massive; friable and hard; common fine and medium mottles of dark yellowish brown (10YR 4/4) and yellowish brown (10YR 5/4), much of the color due to staining by concretions; many black and brown iron-manganese concretions up to 1/2" in diameter; pH 5.5; abrupt wavy boundary.

- B21t 30-38¹¹ Mottled light gray (10YR 7/2 moist), gray (10YR 5/1 moist), light yellowish brown (10YR 5/6 moist) silty clay loam, weak coarse blocky to massive; firm and hard; cleavage planes break easily but are very weak; this continuous clay skins on both horizontal and vertical faces; some concretions; many pipestems and channels of pale brown very fine sand and silt are found throughout the horizon; pH 6.6; grades to horizon below.
- B22t 38-54¹¹ Mottled colors as above, but mottles are coarser; silty clay; weak coarse blocky to massive, very firm and very hard; very few cleavage planes, but thick distinct clay skins are continuous on all peds; few concretions; pipestems of pale brown very fine sand and silt very pronounced but end in lower portion of horizon; pH 7.3; diffuse wavy boundary.
- B23t 53-64¹¹ Mottled colors as above, but not as coarse, silty clay loam, massive; slightly firm and hard; common weak patchy clay skins; few concretions, pH 7.2; diffuse boundary.
- B31 64-80¹¹ Strongly mottled brownish yellow (10YR 6/8), yellowish brown (10YR 5/8) and very pale brown (10YR 7/3) clay loam; massive; firm and hard; much of the horizon is made up of black and brown ferromanganese material that is soft when moist; it appears as large patches in the soil mass and also coats parts of other soil material; pH 7.4; gradual boundary.
- C 80-90¹¹⁺ Strongly mottled yellow (10YR 7/8), brownish yellow (10YR 6/8), dark brown (10YR 4/3), black (10YR 2/1) and very pale brown (10YR 7/3) more and brighter yellows than horizon above, clay loam; massive; firm and slightly hard, much ferro-manganese material, like above; pH 7.4 Probably weathered soft silty shales or siltstones.

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