ACID CHARACTER OF SAUCONITE: INCREASE IN CATION EXCHANGE CAPACITY ON AGING IN WATER AND THE ROLE OF Zn^{2+} AND Al^{3+} IONS

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Abstract—pH- and conductometric titration curves of acid sauconite, freshly prepared by the action of H-resin on sauconite showed four segments, each, where H^+, Al^{3+} and Zn^{2+} ions and a weak acid reacted with the added base in the sequence mentioned. The H^+, Al^{3+} and Zn^{2+} ions, but not the weak acid, could be exchanged for the cations of a neutral salt. The exchangeable Al^{3+} and Zn^{2+} ions were derived from the lateral surfaces by the action of the H-resin. When the acid sauconite was allowed to age in water, the exchangeable H^+ and Al^{3+} ions were gradually replaced by Zn^{2+} ions giving, finally, a Zn-clay. The pH rose from 4·2 to 6·3 and the total amount of exchangeable cations increased as aging proceeded. When the Zn-clay was formed, the increase in cation exchange capacity was about 70 per cent. Octahedral Al at the edges, carrying positive charges, were discharged by hydrolysis during the aging, causing the net negative charge and, hence, cation exchange capacity, to increase. Aging had little effect on the amount of the weak acid. Zn and Al ions at the edges exhibited the weak acid function. Only edge-Zn was active in the fully aged clay.

INTRODUCTION

FROM THE results of chemical analyses of several zinc-bearing clays and their examination by thin section-microscopy, X-ray diffraction and differential thermal analyses, Ross (1946) concluded that they constituted a clay mineral of the montmorillonite group, sauconite, a name given earlier to a zinc-bearing clay from Saucon Valley, near Friedensville, Pennsylvania, U.S.A. Sauconite is an uncommon clay mineral. The literature makes no reference to any previous work on its cation exchange behavior and acid character. We have made a titrimetric study of these aspects using acid sauconite prepared by the action of H-resin on sauconite. pH- and conductometric titrations have been done on freshly prepared as well as aged acid sauconite. Neutral salt extracts of the acid clay have been titrated for exchangeable cations. Considerable attention has been given to the manner in which the titration behavior of acid sauconite is influenced by Zn^{2+} and Al^{3+} ions. The latter ions migrate to occupy exchange sites after mobilization from the lateral surfaces of the sauconite crystals by the action of H-resin as well as during the aging of the acid sauconite in water.

EXPERIMENTAL

The starting material* was a brown clay from

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*Obtained from Dr. C. S. Ross through the courtesy of Dr. M. V. Rao.

Arkansas described as sample No. 4 by Ross (1946). It was available as small granules which had to be given a mild grinding in an agate mortar in order to get a sufficiently stable suspension in water from which the $2·0\ \mu$ fraction of the clay was isolated. This fraction was repeatedly leached with a solution of 1·0N NaCl to convert it into Na-clay. The latter, washed free from Cl ions, was suspended in water and passed through columns of H-resin (IR-120 Amberlite) to obtain acid sauconite. One portion was used for immediate (0 hr) titration while the other portion was allowed to age in water for different periods of time at the end of which samples were taken out for titration. Details of the titration procedure have been given elsewhere (Mitra and Kapoor, 1969). Polarograms of neutral salt extracts, with a view to estimating Zn^{2+} ions in the latter, were taken on a recording Hungarian polarograph (OH-102). The cation exchange capacity (CEC) of the $2·0\ \mu$ fraction (not treated with H-resin) was determined by repeatedly leaching it with a neutral 1·0N solution of $BaCl_2$ and then estimating the adsorbed Ba^{2+} ions as $BaSO_4$ after extraction with a 1·0N solution of NaCl.

RESULTS AND DISCUSSION

(a) *Freshly prepared acid sauconite (0 hr sample)*

Titration curves obtained with freshly prepared acid sauconite are given in Fig. 1. The pH titration curve *a*, shows four inflections, following a buffer
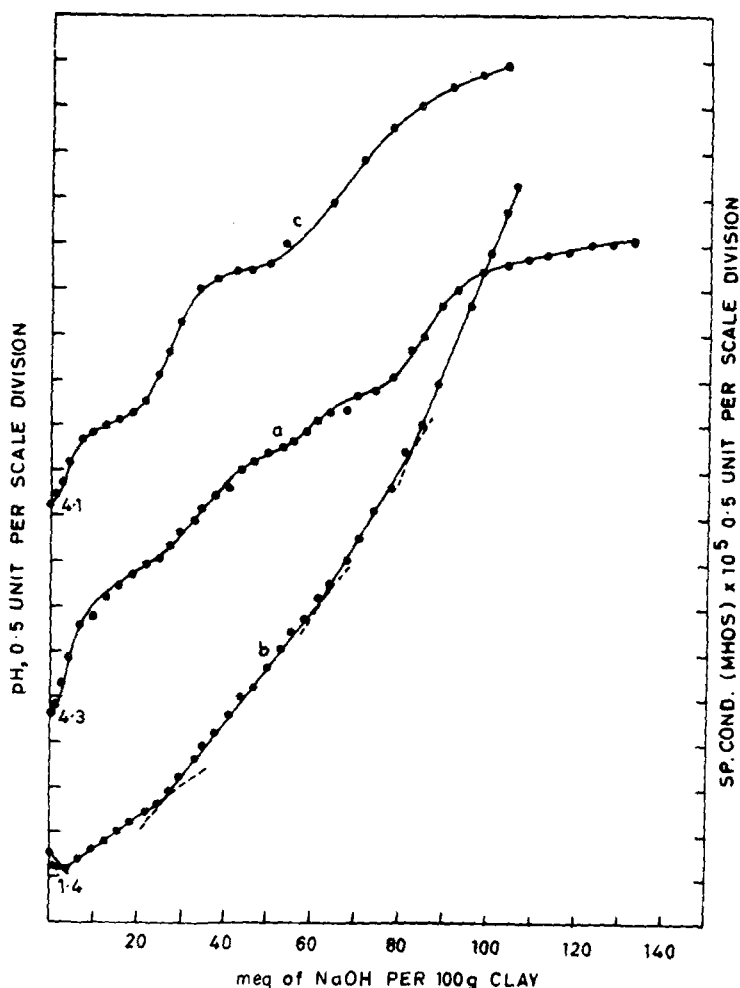
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Fig. 1. pH- and conductometric titration curves of freshly prepared acid sauconite; (a) pH; (b) Cond.; and (c) pH (neutral salt extract). Initial pH/conductance is indicated on the curves.
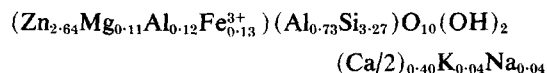
range, each. The conductometric titration curve *b*, has four corresponding breaks. The pH titration curve *c*, of the neutral salt extract shows three buffer ranges and three inflections. At the third or final inflection of this titration curve, 60 meq of the base are used up in reactions with (acidic) cations which have been exchanged for the Na^+ ions of the salt. Of these, strong H^+ ions make 5 meq and they are neutralized at the first inflection in the titration curve of the salt extract. The other exchangeable cations are Al^{3+} and Zn^{2+} ions. 25 meq and 30 meq, respectively, of these ions react with the base in the second and third buffer ranges of the titration curve. Comparison of the polarogram of the salt extract with the polarograms of standard solutions

of $ZnCl_2$ showed that 30 meq of Zn^{2+} ions were present in the extract.

In the first three buffer ranges of the pH titration curve of the acid sauconite, H^+, Al^{3+} and Zn^{2+} ions react with the base in the order mentioned, their amounts being the same as those found in the salt extract. The first three segments of the conductometric titration curve have the same significance.

The exchangeable H^+, Al^{3+} and Zn^{2+} ions balance negative charges caused by the isomorphous replacements of cations within the sauconite lattice. Acid montmorillonite freshly prepared by the action of H-resin on montmorillonite is known to contain exchangeable H^+ and Al^{3+} ions (Lai, Mortland and Timnick, 1957; Aldrich and

Buchanan, 1958; Mitra and Singh 1959; Thomson and Culbartson, 1959). In the acidic environment provided by the H-resin, Al^{3+} ions are mobilized from the edges of the crystals, which then proceed to occupy the exchange sites. According to the formula

$$(Zn_{2 \cdot 64}Mg_{0 \cdot 11}Al_{0 \cdot 12}Fe^{3+}_{0 \cdot 13})(Al_{0 \cdot 73}Si_{3 \cdot 27})O_{10}(OH)_2$$
$$(Ca/2)_{0 \cdot 40}K_{0 \cdot 04}Na_{0 \cdot 04}$$

of the brown clay given by Ross (1946), Zn^{2+} ions occupy octahedral positions together with small amounts of Al^{3+} (and Fe^{3+}) ions, some Al^{3+} ions also replacing Si^{4+} ions in the tetrahedral layer. By the action of the H-resin, Zn^{2+} and Al^{3+} ions are dislodged from the lateral surfaces and then occupy the exchange sites.

The presence of Al^{3+} (and Fe^{3+}) ions in the octahedral layer gives a positive charge to this layer which is, however, offset by the negative charge created in the tetrahedral layer by the replacement of Si^{4+} by Al^{3+} ions. The net charge is negative. According to the formula given by Ross, it is about 50 meq per 100 g of the clay. The amount (60 meq per 100 g) of exchangeable cations found in the neutral salt extract is somewhat larger than this value. The increase in the amount of exchangeable cations in the clay following the H-resin treatment signifies a corresponding increase in its net negative charge and it shows, further, that the exchangeable Al^{3+} ions which are found in the acid sauconite have been derived by a dissolution, by the action of the H-resin on the clay, of the octahedral Al at the edges in preference to tetrahedral Al. This aspect has been further discussed in the next section.

Beyond the third inflection/break in the titration curve of the acid sauconite and up to the fourth inflection/break, 20 meq of a weakly acidic species react with the base which is not found in the neutral salt extract. Resin-treated montmorillonite, also, has been found to contain a similar weak acid

component, which could not be extracted by the solution of a neutral salt (Mitra, Sharma and Kapoor, 1963; Mitra and Kapoor, 1969). The following would be a plausible mechanism of the observed weak acid function of acid sauconite: The Zn^{2+} and Al^{3+} ions exposed on the lateral surfaces carry some residual positive charge. Due to lattice terminations, these surfaces will have both positive and negative centres on them. When the clay is suspended in water and the pH is low, as is the case with acid sauconite, an exposed positively charged cation of the octahedral layer will complete its octahedral shell with water molecules. In a titration of the acid clay, when all the exchangeable H^+, Al^{3+} and Zn^{2+} ions have reacted with the base and more of the latter is added, OH' ions displace the water molecules from the octahedral shell of the Zn^{2+} and Al^{3+} (Fe^{3+}) ions at the edges and the cations of the base balance the negative centres present on the lateral surfaces. The exposed Zn^{2+} and Al^{3+} (Fe^{3+}) ions, in effect, act as a Lewis acid and they are responsible for the weak acid function of the acid sauconite.

(b) Effect of aging

pH- and conductometric titration curves of acid sauconite, which was allowed to age in water for different periods of time before titration, are given in Figs. 2 and 3, respectively. Figure 4 shows the pH titration curves of the neutral salt extracts of the aged samples. Base combining capacities (BCC) at the inflections/breaks of the titration curves given in Figs. 2–4 are shown in Table 1. Results of polarographic estimation of Zn^{2+} ions in the salt extracts are given in the last column of the table.

The three sets of titration curves (and Table 1) show that (exchangeable) strong H^+ ions disappear after one day's aging. The pH also increases from $4 \cdot 3$ to $4 \cdot 6$ during this period. On further aging, exchangeable Al^{3+} ions disappear. The H^+ and Al^{3+} ions are replaced by Zn^{2+} ions and after 15

Table 1. Base combining capacity (meq/100 g) of acid sauconite and its content of exchangeable Zn^{+2} ions after different periods of aging

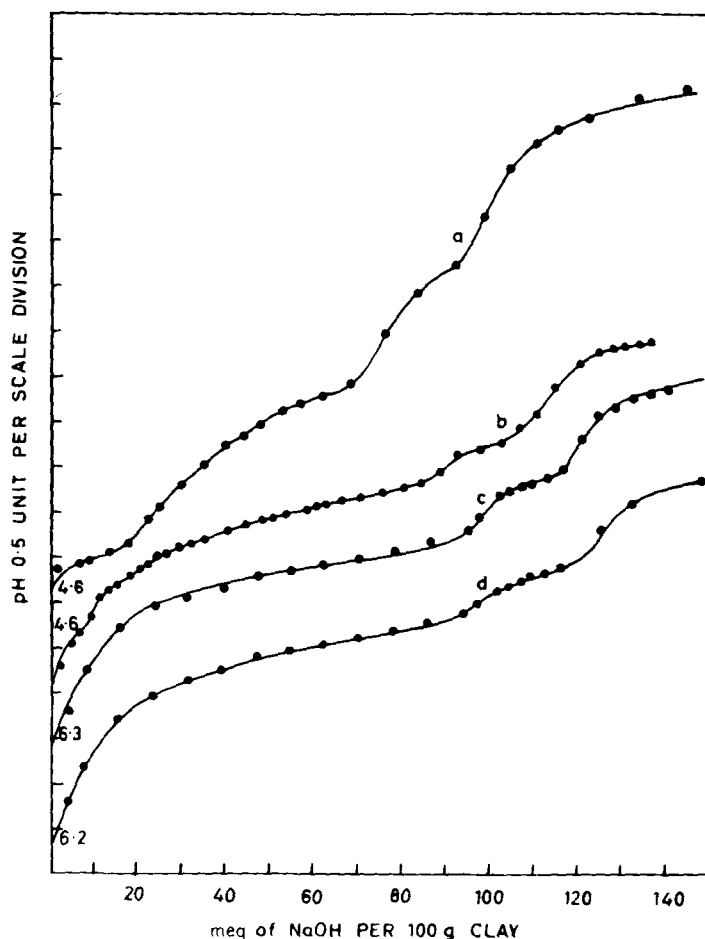| Aging time	Acid clay conductivity curve (break)				Acid clay pH curve (inflexion)				Salt extract pH curve (inflexion)				Zn^{2+}*
	1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th	
0	5	25	60	80	5	30	60	80	5	30	60		30
1 day	20	70	90		20	70	95		20	75			50
4 days	10	90	110		10	90	110		90				80
15 days	100	120			100	120			100				95
3 months	100	120			100	125			95				95

*Determined polaragraphically.

Fig. 2. pH titration curves of acid sauconite; (a) aged for 1 day; (b) aged for
4 days; (c) aged for 15 days; and (d) aged for 3 months.

days' aging, only Zn^{2+} ions are found in the salt extract.

Replacement of strong H^+ ions in acid montmorillonite by Al^{3+} ions during aging is well known (Harward and Coleman, 1954; Coleman and Craig, 1961; Schwartmann and Jackson 1963; Mitra and Kapoor, 1969). The strong H^+ ions which are located on the planar surfaces attack Si–O–Al bonds at the edges or lateral surfaces either during collision between the two kinds of surfaces in the course of the Brownian motion of the crystallites (Mitra and Singh, 1959) or as a result of diffusion to the sites of the Si–O–Al bonds at the edges of the same crystal (Eckman and Laudelout, 1961). Al^{3+} ions, which are released thereby, displace the strong H^+ ions. The latter, after attacking the Si–O–Al bonds, are converted into very weakly acidic SiOH groups which would not react appreciably with a base below pH 10·5. In the case of acid sauconite, the strong H^+ ions also attack Si–O–Zn bonds, mobilizing Zn^{2+} ions which then replace the former. The fact that freshly prepared acid sauconite already contains eschangeable Al^{3+} and Zn^{2+} ions shows that similar proton attack on Si–O–Al and Si–O–Zn bonds had taken place in contact with the resin phase; protons, then, were available from the resin, in addition to protons which had already entered the clay phase in exchange for cations like Na^+ and Ca^{2+}. When the clay is allowed to age alone, the latter category of protons are available for mobilizing Al^{3+} and Zn^{2+} ions from the edges. These protons combine with OH groups attached to edge Al's and Zn's, besides attacking the Si–O–Al and Si–O–Zn bonds. All these proces-
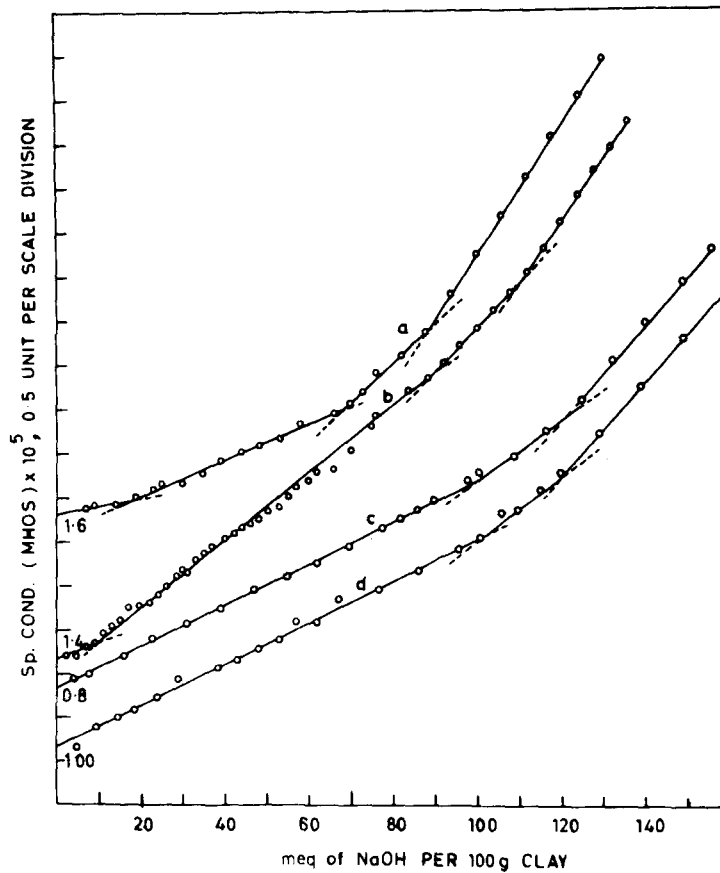
Fig. 3. Conductometric titration curves of acid sauconite; (a) aged for 1 day; (b) aged for 4 days (c) aged for 15 days, and (d) aged for 3 months.

ses cause the pH to rise. Al^{3+} ions would not be stable in solution above pH 4·5. Hence, as the pH rises and approaches this value, Al^{3+} ions which have already moved from the edges and exchanged sites with strong H^+ ions are precipitated as $Al(OH)_3$. Zn^{2+} (and $ZnOH^+$) ions are, however, stable in solution up to a pH of about 6·5. Accordingly, Zn^{2+} ($ZnOH^+$) ions continue to be mobilized from the edges and take the place of exchangeable H^+/Al^{3+} ions. The protons generated by the hydrolysis of exchangeable Al^{3+} ions contribute towards the mobilization of Zn^{2+} and the ultimate product is a Zn–clay.

If only exchangeable (strong) H^+ ions and protons produced by the hydrolysis of exchangeable Al^{3+} ions were responsible for the mobilization of Zn^{2+} ions from the edges, the total quantity of H^+, Al^{3+} and Zn^{2+} ions in the neutral salt extract would be the same irrespective of the age of the clay, though the relative amounts of these cations in the extract would vary. Indeed, in the case of acid montmorillonite where the only exchangeable cations are H^+ and Al^{3+} ions, the total quantity of these two cations remains constant during aging (Mitra and Kapoor, 1969) though H^+ ions are gradually replaced by Al^{3+} ions as aging proceeds. Acid sauconite differs from acid montmorillonite in this respect. The titration curves given in Figs. 2–4 (and Table 1) show that after the acid sauconite has aged for 15 days, the amount of exchangeable Zn^{2+} cations in the (homoionic) Zn-clay which is now formed, is about 66 per cent larger than the total quantity of exchangeable H^+, Al^+ and Zn^{2+} ions in the freshly prepared acid sauconite. This is a novel feature and it shows that Zn^{2+} ions are mobilized by protons derived from some other source, especially, above pH 4·5. It is possible that between pH 4·5 and 6·5, Al^{3+} ions at the edges
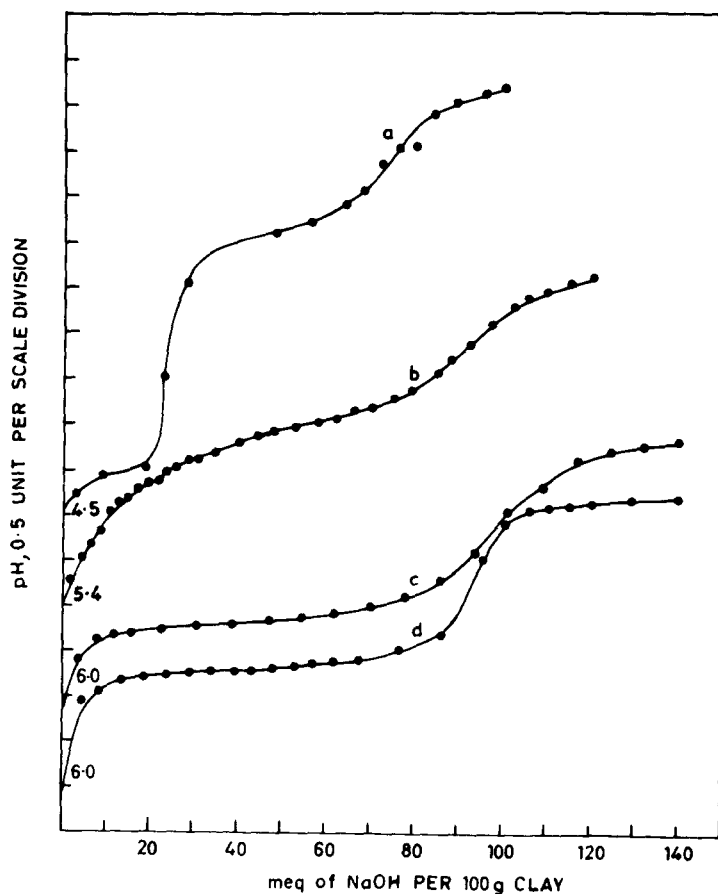
Fig. 4. pH titration curves of salt extracts of acid sauconite; (a) aged for 1
day; (b) aged for 4 days; (c) aged for 15 days; and (d) aged for 3 months.

hydrolyze to furnish protons which then attack Si–O–Zn bonds, giving practically undissociated Si–O–H groups and free Zn^{2+} ions. The latter balance the negative charge which the exposed Al^{3+} ions neutralized before they were discharged by the uptake of OH ions during hydrolysis. The liberated Zn^{2+} ions become available for exchange with the cations of the salt. Table 1 shows that the amount of Zn^{2+} ions in the salt extract reaches a limiting value after 15 days' aging and there is no further increase if the clay is allowed to age for 3 months. The limit seems to be reached when all exposed Al^{3+} ions at the edges have been hydrolyzed giving protons for the mobilization of the Zn^{2+} ions.

Hydrolysis of the edge aluminums would annul their weak acid function referred to above. However, there would still be many Zn^{2+} ions at the edges which would act as a nonextractable Lewis acid. They would account for the second buffer range in the titration curve of acid sauconite after it has aged for 15 days or more.

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Résumé – Les courbes de titration acidimétriques (pH) et conductimétriques d'une sauconite acide, fraîchement préparée par action d'une résine H sur une sauconite montrent quatre segments à l'intérieur desquels la base ajoutée réagit successivement et dans l'ordre avec les ions H^+, Al^{3+}, Zn^{2+} et un acide faible. Il est possible d'échanger contre les cations d'un sel neutre les ions H^+, Al^{3+} et Zn^{2+}, mais pas l'acide faible. Les ions échangeables Al^{3+} et Zn^{2+} proviennent des surfaces latérales à cause de l'action de la résine H. Quand on laisse la sauconite acide vieillir dans l'eau, les ions échangeables H^+ et Al^{3+} sont graduellement remplacés par les ions Zn^{2+}, ce qui donne finalement une argile Zn. Le pH s'élève de 4,2 à 6,3 et la quantité totale de cations échangeables augmente quand le vieillissement progresse. Quant l'argile Zn est formée, l'augmentation de la capacité d'échange est d'environ soixante dix pour cent. Les ions Al octaédriques des bords, qui portent des charges positives, sont déchargés par l'hydrolyse pendant le vieillissement, ce qui entraîne une augmentation de la charge négative nette, et donc, de la capacité d'échange cationique. Le vieillissement a peu d'effet sur la quantité d'acide faible. Les ions Zn et Al situés sur les bords possèdent la fonction acide faible. Seul Zn des bords est actif dans l'argile qui a subi un vieillissement total.

Kurzreferat – pH und konduktometrische Titrationskurven eines sauren Sauconits, frisch bereitet durch die Einwirkung von H-Harz auf Sauconit, ergaben jeweils vier Abschnitte, wo H^+, Al^{3+} und Zn^{2+} sowie eine schwache Säure mit der zugefügten Base in der erwähnten Reihenfolge reagierten. Die H^+, Al^{3+} und Zn^{2+} Ionen, jedoch nicht die schwache Säure, konnten gegen die Kationen eines Neutralsalzes ausgetauscht werden. Die austauschfähigen Al^{3+} und Zn^{2+} Ionen wurden aus den seitlichen Oberflächen durch Einwirkung des H-Harzes erhalten. Bei Alterung des sauren Sauconits in Wasser wurden die austauschfähigen H^+ und Al^{3+} Ionen allmählich durch Zn^{2+} Ionen ersetzt um schlussendlich einen Zn-Ton zu liefern. Das pH stieg an von 4,2 auf 6,3 und die Gesamtmenge an austauschbaren Kationen nahm mit fortschreitender Alterung zu. Bei der Bildung des Zn-Tones war die Zunahme im Kationenaustauschvermögen etwa siebzig Prozent. Oktaedrische Al an den Kanten, mit positiven Ladungen behaftet, wurden im Laufe der Alterung durch Hydrolyse entladen wodurch die negative Nettoladung, und somit die Kationenaustauschfähigkeit, zunahm. Die Alterung hatte wenig Einfluss auf die Menge der schwachen Säure. Zn und Al Ionen an den Kanten zeigten schwach saure Funktion. Im voll gealterten Ton war nur das Kanten-Zn wirksam.

Резюме — Кривые титрования (измерение pH и проводимости), которые получены для кислого соконита, приготовленного воздействием H-смолы на соконит, имеют четыре сегмента, в пределах которых ионы H^+, Al^{3+} и Zn^{2+} и слабая кислота взаимодействовали с добавленным основанием в указанной последовательности. Ионы H^+, Al^{3+} и Zn^{2+} могут обмениваться на катион нейтральной соли, но слабая кислота не обнаруживает этого свойства. Обменные ионы Al^{3+} и Zn^{2+} удалялись с боковых поверхностей взаимодействием с H-смолой. При старении кислого соконита в воде обменные ионы H^+ и Al^{3+} постепенно замещались на Zn^{2+}, что приводило в конечном итоге к образованию Zn–глины. В процессе старения значение pH возрастало с 4,2 до 6,3 и увеличивалось общее количество обменных катионов. При образовании Zn–глины увеличение катионо-обменной емкости составляло около 70%. Октаэдрические катионы алюминия, создающие положительный заряд на ребрах, теряли заряды в процессе старения вследствие гидролиза; это приводило к появлению отрицательного заряда и, как следствие, к увеличению катионо-обменной емкости. Старение оказывает лишь незначительное влияние на количество слабой кислоты. Ионы Zn и Al на ребрах обнаруживают слабо кислые свойства. В глине, полностью прошедшей процесс стареиня, активными былишь ребра с катионами Zn.