

# KINETICS OF REACTIONS IN THE CONVERSION OF Na- OR Ca-SATURATED CLAY TO H-AL CLAY

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## ABSTRACT

H-ION was added to Na or Ca bentonite suspensions. The H-ion was added either in solution, as HCl, or adsorbed on a cation exchange resin. The variation with time of the quantities of H and Al in various phases of the system was determined.

In the first stage of the reaction both exchangeable H and exchangeable Al on the clay increased rapidly. Several facts showed that the exchangeable Al was not liberated by crystal structure decomposition. It is postulated that its appearance is the result of a rapid dehydroxylation, of hydroxy Al groups located at plate edges or adsorbed on basal planes, producing water and trivalent Al ions.

During the second stage of the reaction, spontaneous self-decomposition of the clay structure takes place. It was found that when the H-clay is alone in suspension or with low concentration of acid, the decomposition stops after the liberation of a limited quantity of Al. Most of this Al is adsorbed on the clay and it becomes the prevailing exchangeable ion. On the contrary, when the H-clay is aging in the presence of H-resin, a system of consecutive reactions is operating. In this system, Al liberated from the structure is transferred to the adsorbed state in the clay and from there to the resin. As a result the decomposition reaction does not stop as in the absence of the resin, but is carried further.

## INTRODUCTION

THE complete process of conversion of clays saturated with metallic cations to clays in the H-Al state basically consists of two groups of reactions: (1) simple ion exchange reactions of hydrogen with metallic cations on the clay surface, and (2) decomposition-exchange of adsorbed H with cations (mainly Al) of the crystal structure. Almost all the work done in this field has dealt with the latter reaction only (Low, 1955; Laudelout and Eeckman, 1958; Eeckman and Laudelout, 1961; Coleman and Craig, 1961; Davies, Turner, and Whittig, 1962). However, no detailed research was done on the relation and interaction between the two aforementioned basic reactions. In order to investigate this aspect, the present work was designed to follow the kinetics and mechanisms of Al changes throughout the whole process of conversion and to study Al participation in both the basic reactions.

## EXPERIMENTAL

*Materials*

*Clay suspensions.*—The  $< 2 \mu$  fraction of Wyoming bentonite (Cenco C-1051) was separated from a 1% suspension of the crude clay by sedimentation and decantation. Then the separated clay was saturated with Na, H, or Ca as follows:

To saturate the  $< 2 \mu$  clay with Na, a suspension of the clay was passed through a Na-saturated exchange resin (Amberlite IR-120) in accordance with the procedure of Bolt and Frissel (1960). Then the free electrolytes were removed by repeatedly filtering out the clay on ceramic filter candles and redispersing it in demineralized water.

Some of the Na-clay was converted to H-clay by passing it through a H-saturated exchange resin. The resulting H-clay was used in the pertinent experiments immediately after preparation. Its concentration in these experiments was the same as that used for the Na- and Ca-clays.

To saturate the  $< 2 \mu$  clay with Ca, it was leached on a Buchner funnel, first with 1 N  $\text{CaCl}_2$  (pH = 3.0) and then with 99% methanol, according to the method of Jackson (1956, p. 801-2). Finally, it was washed with water, by using the filter candles, as before.

Both the Na and Ca clay stock suspensions were brought to a concentration of 5.65 g of oven dry clay per liter of suspension. The exchange capacity of the clay was 82 meq/100 g.

*Cation exchange resin.*—Before being used, the hydrogen Amberlite (IR-120 AR) was leached with demineralized water to remove any decomposition products. This procedure was repeated every two weeks. After leaching, the excess water was removed by applying suction. However, this treatment did not dry the resin completely. Consequently, no delay in the exchange reaction, due to hydration of the resin, occurred when it was added to the clay suspension.

Always the resin was added in the same amount, namely, 0.500 g (oven dry basis) per experiment. The same batch of resin was used throughout. It was regenerated periodically by leaching it with 1 N HCl. The exchange capacity of the resin was 4.70 meq/g.

*Methods*

Two different experimental systems were used to follow the conversion of the clay to the H-Al state. These are described below.

*Clay-resin systems.*—A 25 ml aliquot of the stock suspension of Na- or Ca-clay, diluted to 50 ml with either demineralized water or salt solution, was brought to the required temperature in a water bath controlled to  $\pm 0.03^\circ\text{C}$ . Then the wet resin was added and the mixture was vigorously agitated in the bath. When the agitation was stopped, after a predetermined contact time, the resin particles settled immediately and the clay suspension

was decanted through a plastic sponge. Thereafter, the resin was washed with demineralized water and the washings were added to the suspension until the volume totalled 100 ml. An aliquot of this suspension was centrifuged to obtain a clay sediment and a clay-free supernatant solution for analysis.

The total meq of H in the suspension were determined in a second aliquot by titrating it conductometrically with NaOH. For this purpose, a constant-delivery-rate burette, a conductivity transducer and a potentiometric recorder were used. The meq of unadsorbed H in the suspension were determined by titrating the clay-free supernatant solution of the first aliquot in the same way. Then the meq of H adsorbed on the clay were obtained by difference.

The resin and clay obtained by sedimentation or centrifugation, as described above, were extracted with 1 N BaCl<sub>2</sub>. The resulting extracts, and also the clay-free supernatant solution, were analyzed for Al by the spectrophotometric method of Wilson and Sergeant (1963). In order to facilitate comparisons, the aluminum in the three phases was reported as meq of Al<sup>3+</sup> per 100 g of oven-dried clay. This is a reasonable basis for reporting since the clay was actually the source of all the Al and since it was found (Banin, 1964) that most of the Al was in the trivalent form.

The above procedure was repeated with several clay-resin mixtures which were allowed to react for different times. Thus, the course of the conversion reaction could be followed.

*Clay-HCl systems.*—A 25 ml aliquot of the freshly prepared suspension of H-clay at room temperature was poured into the same volume of HCl solution in a water bath at the required temperature. After agitating the suspension in the bath for a pre-determined time, the clay was separated from the solution by centrifugation. Thereafter, the procedure for determining H and Al on the clay and in the supernatant solution was the same as that described previously. As in the case of the clay-resin systems, the course of the conversion reaction in the clay-HCl systems was followed by allowing different samples to react for different times. In both systems the effects of free-electrolyte concentration and of temperature were studied using the techniques already described.

## RESULTS

Curves showing changes in Al content with time in both phases of the clay-HCl systems are given in Fig. 1. Note that the exchangeable Al increased with time from an initial low value until it almost saturated the exchange capacity (Fig. 1, II). The total Al in both phases increased correspondingly. The addition of HCl increased the rate of appearance of the Al.

Figures 2, 3, and 4 show the change in Al content with time in the various phases of the clay-resin system. In this system, as in the clay-HCl system, there was a tendency for the total Al (the sum of the meq of Al found by analysis in the supernatant solution and on the exchange complexes of clay

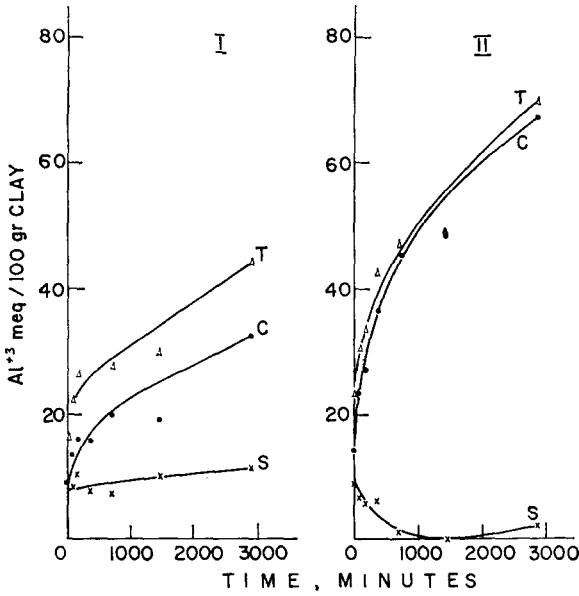


FIG. 1. The effect of reaction time in the clay-HCl system on the aluminum found on the exchange complex of the clay (C), in the solution (S), and in both phases (T) at a reaction temperature of 60°C and an added HCl concentration of (I) 0 meq/L, and (II) 2.5 meq/L.

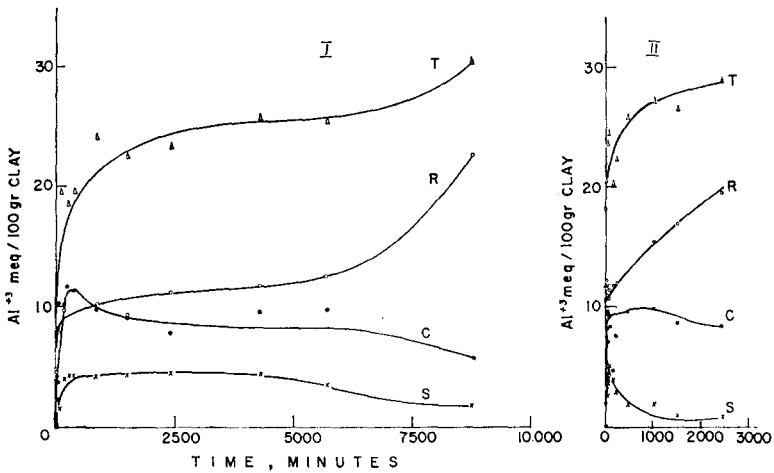


FIG. 2. The effect of reaction time in the Ca-clay-resin system on the aluminum found on the clay (C), on the resin (R), in the solution (S) and in all three phases (T), at a reaction temperature of 25°C and an added  $CaCl_2$  concentration of (I) 0.25 meq/L, and (II) 2.5 meq/L.

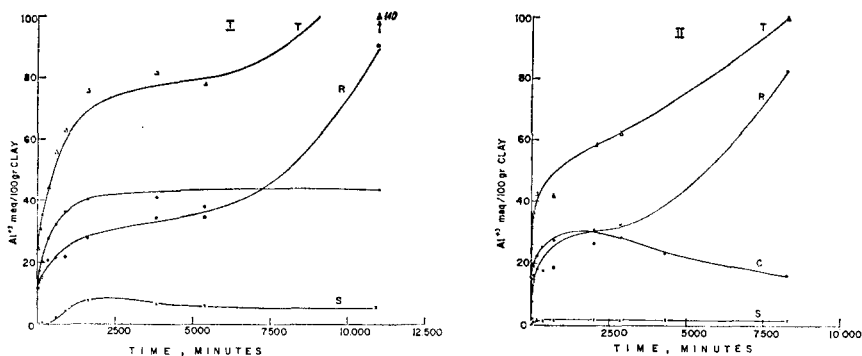


FIG. 3. Variation of aluminum content with reaction time in the Ca-clay-resin system (symbols as in Fig. 2) at a reaction temperature of 60°C and added CaCl<sub>2</sub> concentration of (I) 0 meq/L, and (II) 2.5 meq/L.

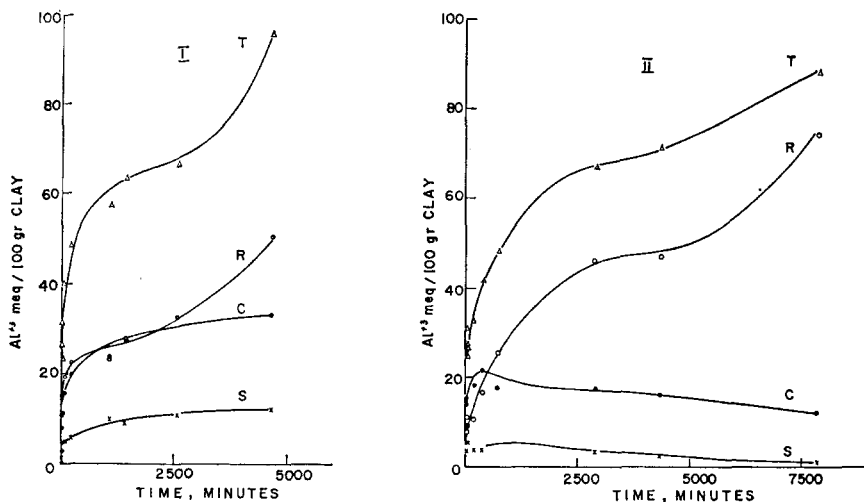


FIG. 4. Variation of aluminum content with reaction time in the Na-clay-resin system (symbols as in Fig. 2) at a reaction temperature of 60°C and added NaCl concentration of (I) 0 meq/L, and (II) 2.5 meq/L.

and resin) to increase with time. However, instead of increasing continuously with time, as in the former case, the exchangeable Al on the clay increased rapidly from zero to a maximum and then decreased. A similar trend was observed for the aluminum in the supernatant solution. The Al on the resin generally increased with time, but there was a period of almost no change followed by a rapid increase. This rapid increase took place at about the time that the exchangeable Al on the clay started to decrease. Temperature elevation caused a significant increase in the total Al, as is evident by com-

paring Figs. 2 and 3. Most of this Al was finally transferred to the resin. The addition of free salt, which results rapidly in free acid by ion exchange with the resin, did not increase the total Al as seen by comparing sections I with II respectively in Figs. 2, 3 and 4. However, it did change the proportions in the different phases, decreasing the amount of exchangeable Al on the clay and increasing the amount of exchangeable Al on the resin. The salt addition also shortened the period after which exchangeable Al on the clay began to decrease.

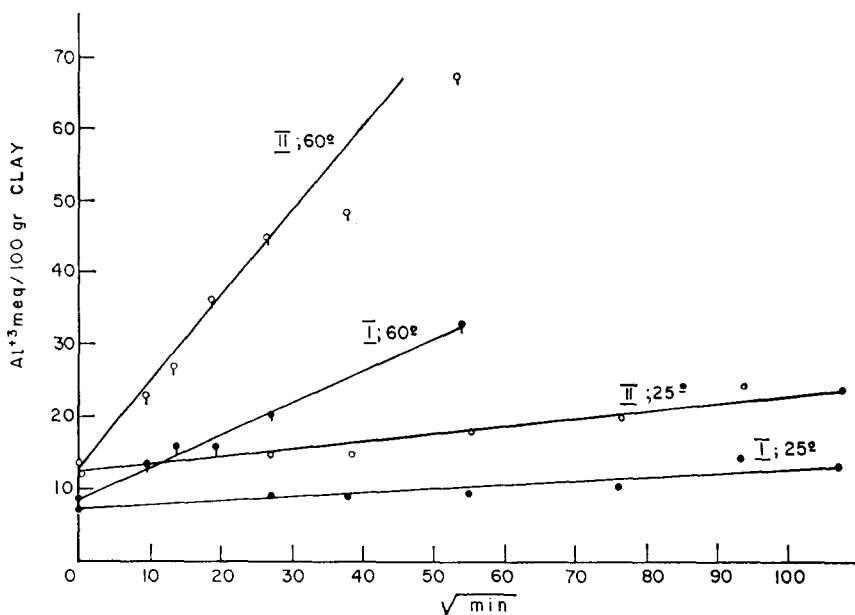


Fig. 5. Exchangeable aluminum on the clay plotted versus the square root of time for the clay-HCl system at reaction temperatures of 25°C or 60°C and added HCl concentration of (I) 0 meq/L, and (II) 2.5 meq/L.

In Fig. 5, exchangeable Al on the clay only is plotted versus the square root of time for the clay-HCl system. In agreement with the results of Eeckman and Laudelout (1961) on the aging of H-Al clay, good linear relationships were observed until the exchangeable Al content became relatively high and approached the exchange capacity of the clay. Then there was some deviation from linearity. The parameters of the equations of the best fitting straight lines are given in Table 1. Evidently, the slopes of the lines were relatively unaffected by changes in electrolyte concentration but were very sensitive to changes in temperature.

Plots of exchangeable Al and exchangeable H on the clay versus the square root of time are shown for the clay-resin system in Fig. 6. Figure 7 is a more

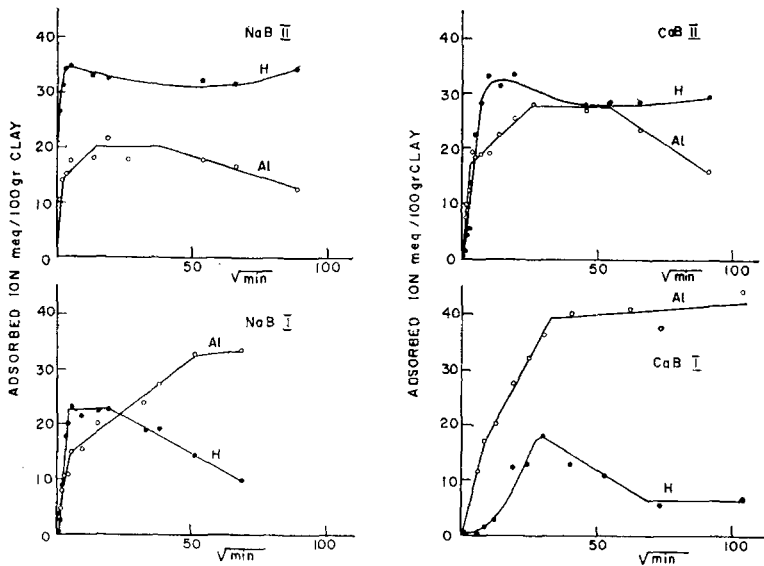


FIG. 6. Exchangeable aluminum and exchangeable hydrogen on the clay plotted versus the square root of time for the clay-resin systems at a temperature of 60°C and added electrolyte concentration of (I) 0 meq/L, and (II) 2.5 meq/L NaCl or CaCl<sub>2</sub> in accordance with the initial exchangeable ion.

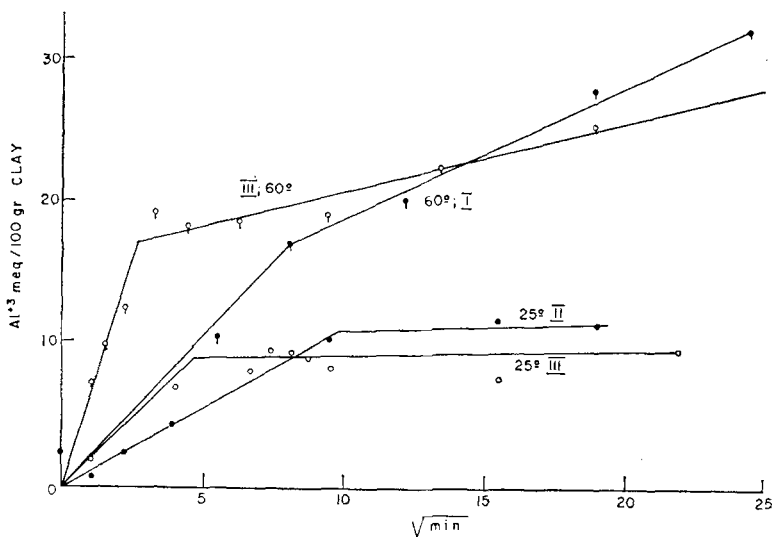


FIG. 7. Exchangeable aluminum on the clay plotted versus the square root of time for the Ca-clay-resin system (details of the initial stage) at reaction temperatures of 25°C or 60°C and added CaCl<sub>2</sub> concentration of (I) 0 meq/L, (II) 0.25 meq/L, and (III) 2.5 meq/L.

TABLE 1.—PARAMETERS OF THE LINEAR EQUATIONS RELATING EXCHANGEABLE Al ON THE CLAY TO THE SQUARE ROOT OF TIME FOR THE CLAY-HCl SYSTEM

Added electrolyte (meq/L)	Temperature (°C)	Intercept (meq/100 g)	Slope (meq/100 g) min <sup>-1/2</sup>
0	25	7.0	0.06
2.50	25	11.9	0.11
0	60	9.0	0.44
2.50	60	14.0	1.16

detailed plot of the exchangeable Al appearing on the clay for reaction times up to about 600 min. It is seen that the Al data for the different experiments can be represented by a series of straight line segments. These line segments are presumed to represent different reactions. The parameters for the line segments corresponding to the first two reactions are given in Table 2.

TABLE 2.—PARAMETERS OF THE LINEAR EQUATIONS RELATING EXCHANGEABLE Al ON THE CLAY TO THE SQUARE ROOT OF TIME FOR THE CLAY-RESIN SYSTEMS\*

Initial metallic cation	Added electrolyte (meq/L)	Temperature °C	First line Segment	Second Line Segment	
			Slope $k'$ (meq/100 g) min <sup>-1/2</sup>	Intercept $b$ (meq/100 g)	Slope $k''$ (meq/100 g) min <sup>-1/2</sup>
Ca	0.25	25	1.1	10.3	0.05
Ca	0.50	25	—	10.7	0.04
Ca	2.50	25	1.8	8.8	0.03
Ca	0	60	2.1	9.8	0.90
Ca	2.50	60	6.5	15.8	0.48
Na	0.40	25	1.9	(8.0)	—
Na	2.50	25	1.8	(10.0)	—
Na	0	60	3.4	11.9	0.50
Na	2.50	60	10.0	15.2	0.33

\* First and second line segments only.

Equation of the first line segment:  $Al = k'\sqrt{t}$

Equation of the second line segment:  $Al = k''\sqrt{t} + b$

In every case, the first reaction ceases or becomes insignificant and the second reaction becomes predominant after a short period of time, not exceeding 100 min. At the point at which the second reaction becomes predominant, the amount of exchangeable Al resulting from the first reaction (obtained from the intercept on the ordinate of the second line segment)



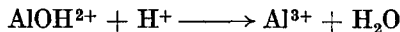
equalled 7–15 meq per 100 g of oven-dried clay. Comparison of the apparent rate of the first reaction in the clay–resin systems with that in the clay–HCl systems shows that the former is relatively high. Further, the rate of the former reaction was much more sensitive to salt addition but less sensitive to changes in temperature. The apparent rate of this reaction was greater for Na-clay than for Ca-clay. While it occurred, the exchangeable H was increasing.

The second and following reactions were much slower than the first, having apparent rates similar to that in the clay–HCl system. The rates of these reactions were increased markedly by an increase in temperature and, in contrast to all the reactions discussed previously, were decreased by the addition of electrolyte. They were not affected by the type of cation initially adsorbed on the clay.

## DISCUSSION

During the first reaction both exchangeable H and exchangeable Al on the clay increased very rapidly. This simultaneous increase of both ions differs from the usual pattern observed in previous works (Low, 1955; Aldrich and Buchanan, 1958; Coleman and Craig, 1961; Eeckman and Laudelout, 1961; Davies *et al.*, 1962). In these works the increase in exchangeable Al was paralleled by a decrease in exchangeable H. Evidently, the first reaction is different from the reactions studied previously. As noted in the results for the clay–resin system, the rate of this reaction was very high, had a small dependence on temperature and a large dependence on electrolyte concentration. These factors distinguished it from subsequent reactions.

Probably, the mechanism of the first reaction can be described as follows: Initially, the clay is saturated with metallic cations. The pH of the suspension is 7.0–8.0. Under these conditions all the Al exposed on surfaces, either at the edges of the plates or as adsorbed polymers on the faces (Shen and Rich, 1962), is in the hydroxy form. In this form the Al is non-exchangeable (Shen and Rich, 1962; Jackson, 1963). At the instant when H appears in the suspension, two reactions occur simultaneously. One is ion exchange of H for the metallic cations on the clay. The other is dehydroxylation of hydroxy-Al polymers and ions, viz.,



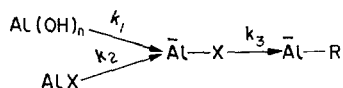
This is the reverse of the hydrolysis reaction. As the  $pK$  of the latter reaction is 5 (Jackson, 1963; Raupach, 1963), the dehydroxylation occurs at a low H concentration—a concentration as low as, or lower than, that required for the ion exchange. Since by their dehydroxylation the Al ions become trivalent and exchangeable, a simultaneous rapid increase in both exchangeable H and Al results.

In this stage Al becomes exchangeable by changing its ionic form and not by liberation from the crystal structure. Therefore, the rate limiting factor is mainly the supply of H to the suspension and not the slow interdiffusion of

ions in the crystal. In the clay-HCl systems the H supply is immediate and the dehydroxylation reaction is so rapid that it can not be followed experimentally. However, its existence in these systems is indicated by the non-zero intercepts on the ordinate in Fig. 5. It occurs at a reduced rate in the clay-resin systems because of the slower release of H from the resin. As this release is facilitated by the addition of salt, the rate of the Al appearance at this stage is also increased by the salt addition, as seen from Table 2. When all the hydroxy Al on the surface has been dehydroxylated the first reaction ceases, and further appearance of exchangeable Al on the clay results from other sources.

During the course of the second reaction in the clay-HCl systems the exchangeable H on the clay declined while the exchangeable Al increased. Evidently, this reaction was the one that has been investigated earlier, namely, the decomposition of the clay structure. The results showed that in this system the decomposition, as measured by the appearance of Al, almost stopped when the clay exchange capacity was saturated with Al. This was so even if the H in the solution was still at a concentration corresponding to pH of 2.6-2.7. On the contrary, it was found that, when the clay was kept in contact with the H resin the exchangeable H on the clay remained high and the exchangeable Al remained low, even at much lower H concentrations (pH = 4.0-4.1). However, exchangeable Al accumulated on the resin. Hence, an additional reaction occurred in the latter system.

The following interpretation of the reactions, subsequent to the first, is proposed: The decomposition of the clay structure is activated by the presence of H adsorbed on the surface. When this H reacts with the structure, Al is liberated and becomes the adsorbed ion on the clay. Being trivalent, the Al is greatly preferred to the H. This means that a small equivalent ionic fraction of Al in the solution is sufficient to keep a high equivalent ionic fraction of Al on the clay, especially if the total electrolyte concentration is low. (The results of Nye *et al.* (1961) on the exchange of Al with another monovalent ion ( $K^+$ ) in a montmorillonite clay illustrate this clearly.) Therefore, at low and moderate H concentrations in solution most of the exchange capacity of the clay can be occupied by Al, although its concentration in the solution might be low. Under these conditions the decomposition process does not proceed because of lack of adsorbed H. On the other hand, when H-resin is present, it will tend to act as a "sink" for the Al and will exchange its H with the Al adsorbed on the clay. Thus, the Al reactions in the clay-resin system can be schematically described as a series of "consecutive reactions":



where  $\text{Al(OH)}_n$ ,  $\text{AlX}$ ,  $\bar{\text{Al}}-\text{X}$  and  $\bar{\text{Al}}-\text{R}$  signify aluminum in the hydroxy form on the surface, in the clay structure, on the exchange complex of the clay,

and on the exchange complex of the resin, respectively. The  $k$ 's are the respective rate constants for the different reactions.

Using the known pattern of concentration changes with time in a series of consecutive reactions the concentration-time curves of the clay-resin system can be interpreted. Reference to Figs. 2, 3 and 4 shows that the exchangeable Al on the clay increased initially, remained essentially constant for a while and then tended to decrease. A maximum in the curve is apparent and is characteristic of an intermediate product in a series of consecutive reactions. Both the location of the maximum, as regards to time, and its magnitude, depend on the ratio between the rates of the reactions producing and consuming the intermediate (Frost and Pearson, 1961, pp. 166-71). Relatively increasing the rate of the producing reaction shifts the maximum to larger time values and higher concentrations. As already noted, temperature elevation increased the maximum concentration. Probably, the rates of both the producing and consuming reactions were increased. But, because of the high energy of activation of the structural decomposition (Eeckman and Laudelout, 1961), which is the main producing reaction, it was the one most affected. On the other hand, relatively increasing the rate of the consuming reaction, will shift the maximum to smaller time values and lower concentrations. Free salt addition had these effects on the maximum concentration of exchangeable Al on the clay. Most likely they were caused by the increased rate of Al transfer from the clay to the resin in the presence of higher electrolyte concentrations.

### CONCLUSIONS

At the very beginning of the process of conversion from metallic cation-saturated clay to H-Al-clay, as soon as the pH of the clay suspension is lowered to the slightly acidic range, exchangeable aluminum appears on the clay as a result of a high rate reaction. This reaction occurs at the same time, or even before, the cation exchange reaction. The appearance of exchangeable aluminum at this stage is not coupled with exchangeable hydrogen loss and does not result from structural decomposition, but is caused by changes in the ionic state of hydroxy-aluminum groups which render their aluminum exchangeable.

At the later stages of the conversion, when the decomposition reaction of hydrogen clay is taking place, the aluminum liberated from the structure is first of all adsorbed on the clay. When the quantity of this adsorbed ion increases it may be dissolved or adsorbed by other ion exchangers present. Only if the clay-adsorbed aluminum is displaced by hydrogen will the decomposition reaction continue.

### ACKNOWLEDGMENT

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