ACID DISSOLUTION OF A TEXAS BENTONITE

by

W. T. Granquist and G. Gardner Sumner

Mellon Institute, Pittsburgh, Pennsylvania

ABSTRACT

Various physical properties of an acid-treated Texas bentonite were studied as a function of treatment time. The observed kinetics were pseudo first-order (large excess of acid) and on this basis and the x-ray results a model and mechanism are proposed that are consistent with observed surface area, exchange capacity, and surface acidity changes. A crude estimation of activation energy gave a value lower than that of Osthaus (1956) but of the right magnitude.

INTRODUCTION

The Fellowship at Mellon Institute sustained by Baroid Division, National Lead Company, is concerned with the physical and chemical properties of the various clay minerals. Recently this interest has been extended to the acid dissolution of the clay minerals largely as a result of the publications of Brindley and Youell (1951), Osthaus (1954, p. 404 ; 1956, p. 301), Packter (1955), Mathers, Weed and Coleman (1955, p. 403), and Kerr, Zimmerman, Fox and Wells (1956, p. 322). This paper reports a study of the acid dissolution of a Texas bentonite in 10 percent hydrochloric acid and confirms and extends the studies of these authors.

The particular clay involved is from Gonzales County, Texas, and is described by Jordan in a private communication as coming from a deposit approximately 12 ft thick in a sediment of Jackson formation, having a 3° dip to the southeast. The crude clay was yellow tan, moist and waxy, uniformly smooth and grit free, but with petrified wood inclusions. The overburden at site of sampling was approximately 5 ft of black sandy clay soil. As will be noted in the results of this investigation, the clay was found to be a (Ca, Mg)–bentonite containing about 15–20 percent cristobalite. The x-ray diffraction data also indicated the probable presence of some subcrystalline material. The cation exchange capacity of the dried crude clay was found to be 76.4 meq/100 g.

This paper presents the experimental procedures, the results of the experimental work, and finally a discussion of these results with particular emphasis on the kinetics of the dissolution. A model is proposed and discussed in the light of the observed kinetics and area changes. The characteristics studied at each treatment time included x-ray diffraction, differential thermal analysis, surface area by nitrogen adsorption, cation exchange capacity and identification of exchange cations, wet analysis, residual acidity, surface acidity and infrared spectra.

292

The reason for attempting the kinetic study was that examination of x-ray diffraction patterns of glycolated specimens indicated a systematic decrease in the intensity of the 17 Å spacing with treatment time. Good diffraction patterns were obtained even up to 77 percent removal of aluminum. It thus seemed that we could follow montmorillonite concentration in this case by observing the change in intensity of this particular peak. This approach was compared with the results of chemical analysis. It will be obvious that many contradictions still exist in the interpretation of our data and we are presenting here more of a progress report than a final answer to the many problems posed by the results of this study.

EXPERIMENTAL PROCEDURES

1. *Acid Treatment*

The ground clay (−200 mesh) was treated with a large excess of 10 percent HCl for varying times. The excess HCl was calculated to be ten times the amount required for complete dissolution of all cationic components of the crude material. Treatment was carried out primarily at reflux temperature, which proved to be 103°C for the boiling clay slurry. Vigorous stirring was used throughout the treatment time. In addition to the run at reflux temperature, data were obtained at 67°C. At the conclusion of a particular treatment time, the clay/acid slurry was poured quickly into a large excess of cold distilled water, the clay allowed to settle, and the supernatant liquid removed by decantation. This type of washing was repeated several times and was followed by filtration on a Buechner funnel to recover the solid phase. The filter cakes were dried at 110°C.

2. *X-Ray Diffraction Procedures*

The samples resulting from the above treatment were first examined by film techniques and then re-examined using diffractometer traces. Each sample was glycolated to a pasty consistency and after the sample holder was loaded face up, the sample was further moistened with a drop of ethylene glycol and smoothed over with a glass slide. Averaged values of the peak heights were obtained by packing and scanning each montmorillonite sample an average of three separate times. The intensities were measured using counts per second corrected for coincidence losses and background. In addition to the intensity study, the widths at half maximum of the 17 Å

peaks were carefully measured using a scanning speed of one-fourth degree per minute. Intensities by this same counts-per-second technique were reported for the 110 montmorillonite peak and the 101 cristobalite peak.

3. *Cation Exchange Capacity and Individual Exchangeable Cations*

The cation exchange capacity of the original clay, and of the treated samples, was determined by using a suitable variation of the ammonium acetate technique (Lepper, 1945). The leachates were examined by flame photometry and by quantitative spectroscopic techniques for Na^+, Ca^{2+}, Mg^{2+} and Al^{3+}. H^+ was determined by washing the treated sample thoroughly with KCl and then titrating the leachate to determine the amount of hydrogen ion removed.

4. *Residual Acidity*

The residual acidity was estimated by boiling a mixture of 0.5 g of sample in ca. 50 ml H_2O, filtering, and titrating with standard NaOH solution. This value was needed for proper interpretation of the H^+ exchange data and the surface acidity values.

5. *Surface Area*

Surface areas were obtained using nitrogen as the adsorbate. These nitrogen areas were determined using standard adsorption apparatus and the results interpreted by the Brunauer–Emmett–Teller (1938) theory.

6. *Differential Thermal Analysis*

The differential thermal analyses were performed in a multiple sample D.T.A. apparatus using a heating rate of 10°C per min. The range investigated was from ambient temperature to 1000°C.

7. *Wet Analysis*

Standard analytical techniques were used to run total analyses on the solid phase from each treatment time.

8. *Surface Acidity*

Surface acidity was investigated using the method of Walling (1950) and Benisi (1956). This technique involved the adsorption of suitable indicators on the anhydrous clay surface and observation of the resulting color. By noting the pK_a of the indicators in the region of color change, a range of pK_a, including the acidity of the clay surface, was obtained. Thus the zero hour sample has a surface pK_a less than $+1.5$ and greater than -3.0.

9. *Infrared Spectra*

The infrared data were obtained from Nujol mulls containing $Pb(SCN)_2$ as an internal standard. The experimental conditions were arranged so that the four traces are roughly comparable and the observed intensity changes reflect changes in OH content.

RESULTS

The collected experimental data appear in Tables 1–4, and in Figs. 1 and 2. These are self-explanatory and discussion is deferred to the next section of the paper.

TABLE 1.—ANALYSIS OF CRUDE BENTONITE AND REACTION PRODUCTS "AS-IS" BASIS

	0	0.75	1.5	3.0	6.0
	Time of Treatment, hr				
% SiO_2 :	63.95	74.65	75.76	79.08	86.47
% Al_2O_3 :	16.23	13.42	13.10	10.13	3.97
% Fe_2O_3	2.72	1.91	2.10	1.66	1.28
% MgO :	3.88	3.06	2.23	1.24	1.00
% Ignition loss :	13.50	7.47	7.12	5.87	4.98
	100.28	100.51	100.31	97.98	97.70

TABLE 2.—VARIOUS PRODUCT CHARACTERISTICS AS A FUNCTION OF TREATMENT TIME

	0	0.75	1.5	3.0	6.0	12.0
	Time of Treatment, hr					
Area of dehydroxylization endotherm, cm^2	7.58	5.37	3.69	4.13	0.96	——
Area (N_2), m^2/g	86	120	126	138	139	112
Residual acidity, percent HCl*	0	0.39%	0.15%	0.04%	0.04%	——
Surface acidity, pK_a	$<+1.5$ >-3.0	<-5.6 >-8.2	<-5.6 >-8.2	<-5.6 >-8.2	<-5.6 >-8.2	<-8.2

* A measure of the acid not removed by the washing procedure.

TABLE 3.—EXCHANGE DATA (ANHYDROUS BASIS) ALL RESULTS REPORTED AS Meq/100 G

	0	0.75	1.5	3.0	6.0
	Time of Treatment, hr				
C.E.C.	76.4	59.4	60.8	53.1	31.8
Na^+	8.05	0.4	0.4	0.4	0.4
Ca^{2+}	42.9	2.6	3.1	N.F.*	N.F.
Mg^{2+}	29.2	3.1	3.4	1.6	0.8
Al^{3+}	1.42	N.F.	N.F.	N.F.	N.F.
H^+	0	36.0	39.6	32.9	13.1

* N.F. = Not Found.

Table 4.—x-Ray Diffraction Data for Treated Samples

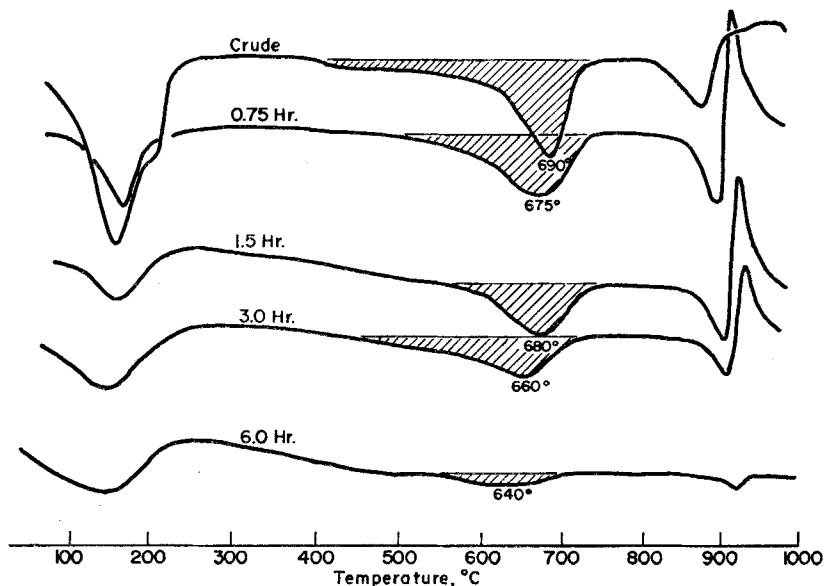|	Treatment Temp., °C	Time of Treatment, hr				
		0	0.75	1.5	3.0	6.0
Peak ht. 001, cps. mont-morillonite $2\theta = 5.2°$	103	455 ± 6	328 ± 42	263 ± 34	148 ± 19	41 ± 7
Peak ht. 110, cps. mont-morillonite $2\theta = 19.8°$	—	116 ± 0	103 ± 8	107 ± 16	106 ± 5	—
Peak ht. 101, cps. cristo-balite $2\theta = 21.7°$	—	205 ± 3	257 ± 3	241 ± 10	253 ± 12	279 ± 9
Width at half-height of 001, mm	—	33	34	35	39	52

Figure 1.—Differential thermal curves demonstrating variation of area of dehydroxyl-ization endotherms with time of treatment.

DISCUSSION OF RESULTS

Kinetics

Osthaus (1956) and Packter (1955) have observed a pseudo first-order reaction for the acid-dissolution of a montmorillonite in excess mineral acid; the results of the present work lead to the same conclusions. It was desired to compare the x-ray approach with the analytical approach, to see if both would yield the same value of the rate constant. For this purpose, an attempt was made to recover the concentration of montmorillonite from the analytical
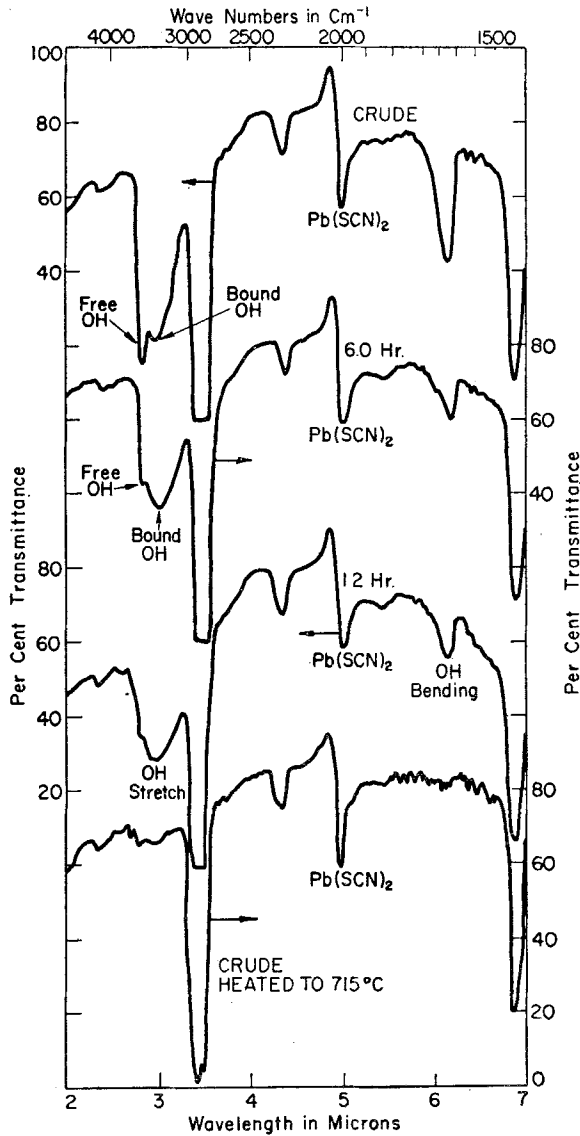
FIGURE 2.—Infrared spectra showing variation of —OH bending and stretching intensities with time of treatment.

data. This was done by assuming that for every Al^{3+}, Fe^{3+} or Mg^{2+} going into solution, 2 Si^{4+} go into an amorphous solid phase as SiO_2. This so-called amorphous solid phase, which need not be physically separated from the unit originally attacked, no longer affects the intensity of the 001 spacing. On this basis, a mass balance was determined for the various stages of the reaction, as shown in Table 5.

TABLE 5.—WEIGHT CHANGES DURING ACID DISSOLUTION OF MONTMORILLONITE

Time, hr	(A) Loss of Al_2O_3 + Fe_2O_3 + MgO	(B) Wt. of SiO_2 Formed	(C) Wt. Solid (C) = 100 − A	(D) Wt. Mont. + Cristobalite (100 − A − B)
0	——	——	100	100
0.75	6.50	13.06	93.50	80.44
1.5	7.55	15.89	92.45	76.56
3.0	12.42	26.59	87.58	60.99
6.0	19.76	40.98	80.24	39.26
12.0	23.66	57.2	76.34	19.1

The integrated intensities were estimated by the product of the peak height and the width at half-height, and intensity ratios (I/I_0) calculated, based on the intensity of the particular reflection in the crude sample. For such relative intensities to be proportional to the fraction of material remaining at time t, a correction must be applied for the loss of solids during the dissolution. It can be shown, assuming constancy of the linear absorption coefficient, that corrected values of relative intensity are obtained by multiplying the experimental values by the fractional weight of total solids, or by column C/100. The weight of montmorillonite was estimated by assuming that the value of 19.1 calculated in Column D for the 12 hr sample was substantially due to cristobalite, since this sample showed no 001 or 110 montmorillonite spacings. $W_{corr.}$ values were obtained by reducing the figures given in Column D by this amount. These corrected values as used in the rate plots are given in Table 6.

TABLE 6.—CORRECTED INTENSITY AND WEIGHT VALUES AS A FUNCTION OF TIME

Time hr	Integrated Intensity, 001 Montmorillonite (Arbitrary units)	I/I_0	$(I/I_0)_{corr.}$	$W_{corr.}$	W/W_0	$\dfrac{C_{Al^{3+}}}{C_{Al^{2+}_0}}$	$(I/I_0)_{corr.}$ cristobalite
0	1.502	1.0	1.0	80.9	1	1	1.0
0.75	1.115	0.745	0.715	61.3	0.76	0.775	1.17
1.5	0.921	0.613	0.561	57.5	0.71	0.755	1.09
3.0	0.577	0.384	0.334	41.9	0.52	0.576	1.08
6.0	0.213	0.142	0.106	20.2	0.25	0.225	1.09

Plots of $\ln(I/I_0)_{corr.}$, $\ln(W/W_0)_{corr.}$ and $\ln(C_{Al^{3+}}/C_{Al_0^{3+}})$ appear in Fig. 3. The slopes of the lines based on W/W_0 and the relative concentration of Al^{3+} in the lattice are about equal, yielding a rate constant of 0.232 hr^{-1}. The slope of the I/I_0 line is considerably greater, giving a rate constant of 0.374 hr^{-1}.
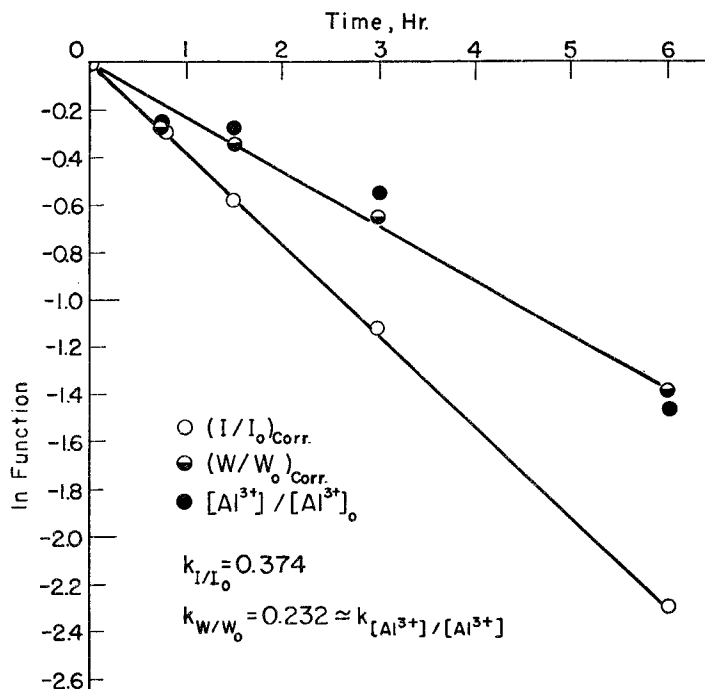

FIGURE 3.—First order rate plots for chemical and x-ray experimental techniques.

It is unfortunate that the rate constants based on the intensity approach and the analytical approach do not coincide because now we must attempt to find the reason for this discrepancy and to decide which technique best describes the kinetics of the dissolution. The most obvious procedure is to consider the original sample as composed of montmorillonite diffracting units and α-cristobalite, as before, plus an additional material, probably amorphous, which is also soluble in the acid. We assume that the analytical procedure measures the change in concentration of both of these materials while the x-ray technique measures only the change in concentration of diffracting units. The difference in rate constants as shown by the plots in Fig. 3 would indicate that the montmorillonite diffracting units are going into solution faster than the total amount of soluble material. This would demand that the subcrystalline phase be less soluble than the montmorillonite as can be shown by the following approach.

We write :

$$\frac{d(x + y)}{dt} = -k_1(x + y)$$

$$\frac{dx}{dt} = -k_2(x)$$

Integrating, solving for t, and equating, we obtain

$$-\frac{1}{k_1} \ln \frac{(x + y)}{(x + y)_0} = -\frac{1}{k_2} \ln \frac{x}{x_0}$$

experimentally, however, $k_2 > k_1$; therefore, $\frac{1}{k_2} < \frac{1}{k_1}$, and

$$-\ln \frac{(x + y)}{(x + y)_0} < -\ln \frac{x}{x_0}$$

or

$$\frac{(x + y)}{(x + y)_0} > \frac{x}{x_0}$$

Cross-multiplying, canceling xx_0, adding $-xy$ to both sides and rearranging :

$$\frac{x_0 - x}{y_0 - y} > \frac{x}{y}$$

$$\left(\frac{x}{y}\right)_{\text{soln}} > \left(\frac{x}{y}\right)_{\text{solid}}$$

If one accepts this postulate of a less soluble subcrystalline material being the cause of the difference in rate constants between the two approaches, it can be concluded that, in this application at least, the intensity technique yields the desired information. Following a review of this paper, Osthaus (private communication) has indicated that the use of his experimental approach might permit the estimation of the amount of amorphous material, and thus bring the intensity and weight plots into coincidence. This has not been attempted.

It might be argued that the subcrystalline material is also montmorillonite. If this were true, such amorphous substance should have a greater surface area than the highly organized montmorillonite and thus be more rapidly attacked by the acid. The experimental results indicate that this is not so. Another possible explanation is that the analytical technique actually measures the rate of dissolution, and that the intensity technique involves the rate of dispersion of aggregates into particles too small to detect by x-ray techniques. Indeed, this may be partly true, but the widths at half-maximum are constant through the three-hour sample, which would seem to contradict such a dispersion process.

The Area Problem

One of the problems in choosing a model for this reaction is that of the change of surface area with time. The model must permit the increase of total surface, but the decrease of reactive surface, as the reaction proceeds. The latter condition is imposed by the observed kinetics. For this reason, and because it seems consistent with the known shape of montmorillonite aggregates, we have selected a cylinder as a model with the axis of the cylinder corresponding to the c-direction (Fig. 4, Model A). Further, we assume the
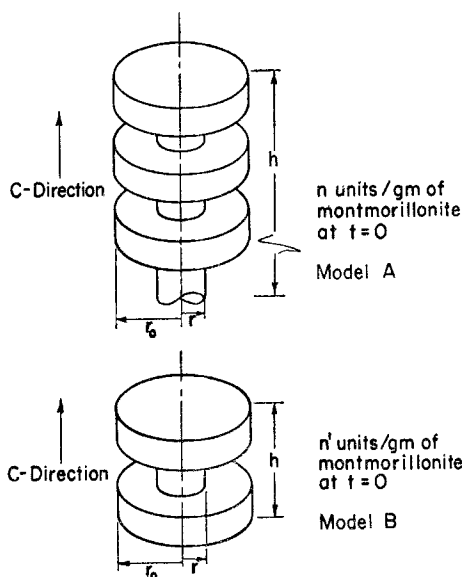

FIGURE 4.—Suggested models for the montmorillonite reactive unit.

height to be constant, owing to the small change in line broadening with treatment time, and the number of such aggregates to remain constant over the course of the reaction.

Then, the attack is assumed to be on the edges of the octahedral layer, resulting in a decrease of octahedral edge area with time, but an increase in total area due to the increasing contribution of exposed tetrahedral face area. The effective reactive unit in terms of the x-ray results at any time is the cylinder defined by the constant height and varying radius of the octahedral layers. The silica may remain attached to this reactive core, giving what might be called an etched cylinder, or separate and build up a separate amorphous phase. Either choice will lead to the same result.

We now investigate the change in total area (S_t) of this model as a function of time. We can consider this area to be made up of end area + octahedral edge area + tetrahedral edge area + tetrahedral face area. Of these, the end

area and the tetrahedral edge area will be constant, while the other contributions will be time dependent. Letting r_0 be the initial radius, h the height, and n the number of units/g at $t = 0$, we write :

$$S_t = n\left[2\pi r_0{}^2 + \frac{4}{3}\,\pi r_0 h + \frac{2}{3}\,\pi r h + 2\left(\frac{h}{10}\right)\pi(r_0{}^2 - r^2)\right],$$

where $\dfrac{h}{10}$ is the number of repeat units along the axis of the cylinder. Experimentally, we know that $r = r_0 e^{-\frac{1}{2}kt}$, where k is the rate constant. Therefore,

$$S_t = n\left[2\pi r_0{}^2 + \frac{4}{3}\,\pi r_0 h + \frac{2}{3}\,\pi r_0 h e^{-\frac{1}{2}kt} + 2\left(\frac{h}{10}\right)\pi r_0{}^2\,(1 - e^{-kt})\right]$$

or rearranging ;

$$S_t = 2\pi n r_0 h\left[2 + e^{-\frac{1}{2}kt}\right] + 2\pi n r_0{}^2\left[1 + \left(\frac{h}{10}\right)e^{-kt}\right]$$

This equation expresses S_t as a function of time and a number of constants. The rate constant can be obtained experimentally, and assumptions can be made about the others. The minimum height for a glycolated unit would be about 1000 Å, but it would be better to assign to h a value of 600 Å, which would represent a dehydrated aggregate.

It must be remembered that the experimental nitrogen areas are expressed in m^2/g of total solids, but our model and method of calculation demand that the area be expressed as m^2/n diffracting units. These n diffracting units weigh 1 g only at $t = 0$. Another correction must also be considered, i.e. the fact that the original sample is not all montmorillonite. Thus, the nitrogen areas should be corrected to a basis corresponding to the initial weight of montmorillonite, which will increase the experimental values. These are then corrected to m^2/n diffracting units by multiplying by the fractional amount of solids based on an original weight of 1 g. Table 7 illustrates these corrections.

TABLE 7.—AREA CORRECTIONS

t hr	Wt. of n units	m^2/g (exp.)	m^2/g (corr.)	m^2/n units
0	1	86	106	106
0.75	0.935	120	148	138
1.5	0.924	126	156	144
3.0	0.875	138	171	149
6.0	0.802	139	172	138

The last column lists the values that must be accounted for by our model.

From considerations of specific volume and N_2 area at $t = 0$, it is possible to estimate r_0 and n, making the assumption that the N_2 area approximates

the surface of the disperse phase in the clay–acid dispersions. This would definitely not be true for sodium–bentonite in water, but is probably a fair guess for (Ca, Mg)–bentonite in 10 percent HCl. The results so obtained, $r_0 = 272$ Å and $n = 3 \times 10^{15}$, are certainly of the right magnitude. At $t = \infty$, however, use of these values in the expression for S_t gives a value of 944 m^2/g. The shape of the curve is qualitatively correct, but the area increases much too rapidly with time. The area obtained at $t = \infty$ is predominantly the area of the tetrahedral faces exposed by the acid treatment and supposes that the face-to-face association of the units in the original aggregate cylinder has not been altered. If such face-to-face association were completely destroyed and the total tetrahedral surface available for adsorption, the area would be twice the $t = \infty$ value. The magnitude checks reasonably well with theoretical values for adsorption areas of montmorillonite as discussed by Grim (1953).

We then must explain why the N$_2$ values do not approach this range, even though the area–time curve is of the same shape. For montmorillonite, N$_2$ cannot penetrate the interlamellar space as can H$_2$O, and it is usually assumed that N$_2$ measures the exterior surface of aggregates. One would expect that the surface developed by the acid treatment would be available, and indeed the surface does increase. The maximum N$_2$ area is only one-sixth that given by the theoretical considerations, and this could be accounted for by assuming that some sort of aggregation occurs during the course of the reaction. For example, is it possible for the freshly exposed tetrahedral surfaces to associate with one another in any way? Since the solution is saturated with respect to SiO$_2$, one possibility is that SiO$_2$ is precipitating from solution as cristobalite, a process made more likely by the initial presence of cristobalite. However, the relative intensities of the cristobalite 101 peaks, corrected for the weight losses occurring during the dissolution, are reasonably constant for the treated sample and only slightly greater than unity (about 1.1).

Another approach to the area problem permits a rather close approximation of the experimental results without the necessity of assigning values to the dimensions of the model, but using the observed first-order kinetics and rate constant and essentially the same model. Here our model is of the shape of one montmorillonite repeat unit, of initial radius r and height h (Fig. 4, Model B). Attack again occurs on the edges of the octahedral layer and the etched sample becomes spool-shaped. The radius of the octahedral layer at time t is r. Finally, there are n' of these diffracting units per gram at time $t = 0$. Then,

$$S_t = 2\pi n' r_0{}^2 + 2\pi n' r \frac{h}{3} + 2\pi n' \, r_0 h \left(\frac{2}{3}\right) + 2\pi n' \, (r_0{}^2 - r^2)$$

$$= 2\,\pi n' r_0{}^2 \left[1 + \frac{1}{3} \frac{r}{r_0} \frac{h}{r_0} + \frac{2}{3} \frac{h}{r_0} + 1 - \left(\frac{r}{r_0}\right)^2 \right]$$

Now, let $\beta = \dfrac{h}{r_0}$ and $\alpha = e^{-\frac{1}{2}kt}$

$$S_t = 2\pi n' r_0{}^2 \left[2 + \frac{1}{3}\alpha\beta + \frac{2}{3}\beta - \alpha^2 \right]$$

$$= 2\pi n' r_0{}^2 \left[2 + \frac{2}{3}\beta + \frac{1}{3}\beta e^{-\frac{1}{2}kt} - e^{-kt} \right]$$

at $t = 0 : S_t^0 = 2\pi n' r_0{}^2 (1 + \beta)$

at $t = \infty : S_t^\infty = 2\pi n' r_0{}^2 \{2 + (2/3)\beta\}$

Therefore :

$$\frac{S_t^\infty}{S_t^0} = \frac{2 + (2/3)\beta}{1 + \beta} = \frac{138}{106} = 1.3$$

and

$$\beta = 1.1$$

Then, since

$$S_t^0 = 2\pi n' r_0{}^2 [1 + \beta] = 106$$
$$2\pi n' r_0{}^2 = 51.0,$$

and the equation becomes, using the experimental value of the rate constant,

$$S_t = 51.0 \, [0.36 \, e^{-0.187t} - e^{-0.374t} + 2.72] = 51.0 \, [A]$$

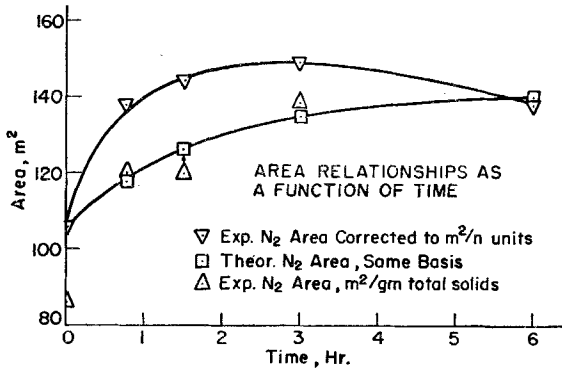Table 8 and Fig. 5 show the results of the calculation.

FIGURE 5.—Comparison of experimental, corrected experimental, and theoretical areas as a function of time.

TABLE 8.—COMPARISON OF THEORETICAL AND OBSERVED AREAS

Time, hr	A	S_t (theor), m^2/n' diff. units	S_t (exp), m^2/n' units
0	2.08	106	106
0.75	2.28	116	138
1.5	2.42	123	144
3.0	2.60	132	149
6.0	2.73	140	138
∞	2.72	139	—

Thus, without assigning values to the unknowns, n, r_0 and h, or considering processes other than montmorillonite dissolution, we can reasonably well reproduce the experimental N_2 area results. The only assumptions were the model and the use of edge attack, plus the experimentally observed kinetics. This might be called the " equivalent spool " approach, and it seems to lend support to the over-all picture of the process.

Mechanism

The reaction is pseudo first-order with respect to the concentration of montmorillonite diffracting units, and the previous section of this paper more completely described our idea of such a unit. Since we start with a given weight of clay in a fixed volume of liquid, the weight of montmorillonite units, W, at any time t, is proportional to the concentration, and we can write

$$- \frac{dW}{dt} = kW,$$

where the rate is defined as dW/dt.

For our model, $W = n\rho\pi r^2 h$ and the reactive surface, S_r, is given by the amount of octahedral edge surface, or $\frac{2}{3} n \pi r h$.

Therefore,

$$\frac{dW}{dt} = - kn \pi r^2 h \rho,$$

but

$$r = \frac{3S_r}{2 \pi n h}$$

and

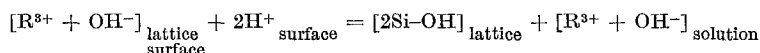$$\text{rate} = - \frac{9 k \rho S_r^2}{4 \pi n h} = -k' S_r^2$$

We must explain as follows this second-order surface dependency to support our assumption of a cylindrical model and edge attack. The excess of H^+ is such that the reaction is independent of the $[H^+]$ in the bulk phase. However, we can assume that the reaction proceeds through H^+ adsorbed on the reactive surface and write the process as

$$[\text{lattice components}]_{\text{surface}} + [H^+]_{\text{surface}} \xrightarrow[H^+]{\text{xs}} \text{Products}$$
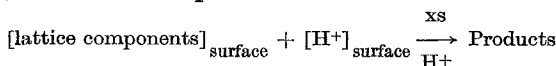
The concentrations of both reactants (lattice components in the surface and adsorbed H^+) are proportional to the surface, and the rate of dissolution thus becomes second order with respect to the reactive surface.

One must also consider the disposition of lattice hydroxyl in the course of the dissolution. We have two sets of data bearing on this problem ; i.e. the infrared spectra and the dehydroxylization endotherms shown on the differential thermograms. The endotherms indicate that the montmorillonite

20

lattice hydroxyl is disappearing in much the same way as the montmorillonite lattice concentration. The intensities of the −OH stretching and bending frequencies do not decrease in this way, however. The intensities are roughly comparable, as demonstrated by the intensities of the internal standard for the various spectra, and show only a gradual decrease with time. These facts can be explained by assuming that lattice hydroxyl is going into solution, but that Si–O resulting from the removal of a cation from the octahedral layer becomes Si–OH. These Si–OH groups will also dehydrate in the course of differential thermal analysis, but at a lower temperature (e.g. note the broadening of the " free-water " endotherm). Ideally, the process would be

$$[R^{3+} + OH^-]_{\substack{\text{lattice}\\\text{surface}}} + 2H^+_{\text{surface}} = [2Si{-}OH]_{\text{lattice}} + [R^{3+} + OH^-]_{\text{solution}}$$

involving a balance electrically. This would cause a decrease in the montmorillonite lattice hydroxyl as given by the D.T.A. endotherms, but an increase in intensity of the —OH frequencies in the infrared spectra. The latter is not observed, and the reaction must be different from the above.

A further factor bearing on this subject is the change in surface acidity and cation exchange capacity with time. The values of the C.E.C. reported earlier must be corrected to a montmorillonite basis. If this is done, the exchange capacity increases with time instead of the decrease shown by the total solids (see Table 9).

TABLE 9.—CHANGES IN EXCHANGE CAPACITY WITH TIME

t, hr	C.E.C., meq/100 g solids (exp)	C.E.C., meq/100 g montmorillonite
0	76.4	94.5
0.75	59.4	97.0
1.5	60.8	105.7
3.0	53.1	127.0
6.0	31.8	157.3

This increase is supported by the observed increase in surface acidity. In order to have an increase in these two properties with time, the reaction must involve a solid phase which becomes more unbalanced electrically as the dissolution proceeds. This charge variation, in turn, implies that octahedral lattice defects are being created, which are not compensated by the transfer of the stoichiometric number of H^+ into the lattice.

Without attempting to write equations for the complex changes occurring, we can describe the reaction as :

lattice components in octahedral edge surface $+H^+$ adsorbed on octahedral edge surface $+$ a large excess of H^+ (aqueous) $=$ hydrated cations in solution $+OH^-$ in solution $+$ lattice at some higher level of charge deficiency balanced by H^+ counter-ions.

From a strictly chemical approach, Kerr *et al.* (1956, p. 322) reach much the same conclusions regarding the attack of protons on the hectorite lattice. Of particular interest is their conclusion that proton attack probably occurs at the edges of the crystals.

Activation Energy

Acid-treatment was also carried out at 67°C in an attempt to estimate the activation energy for the dissolution. The intensity data are given in Table 10.

TABLE 10.—RELATIVE INTENSITY DATA AT $T = 67°C$

t hr	I/I_0
0	1
1.5	0.605
3.0	0.657
6.0	0.365
12.0	0.258

The values are not as nicely linear as was the case at reflux temperature. Nevertheless, the rate constant, $k_{67°}$, was calculated from a straight-line plot, and found to be 0.140 hr^{-1}. The activation energy was estimated from these two points by use of the integrated Arrhenius equation in the form :

$$\frac{\Delta \ln k}{\Delta (1/T)} = \text{slope} = -E_a/R$$

The result was 7.27 kcal/mole, which is substantially lower than that found by Osthaus (1956) using an analytical approach. Estimation of activation energy by such an analytical approach would be of interest in this case, but the necessary data for the 67° series are not available. Extension of the study to other temperatures, thus providing more than two points on which to base the calculation, would undoubtedly improve the agreement. Of particular interest would be the use of moderate pressures to permit dissolution studies at temperatures above reflux.

REFERENCES

Benisi, H. A. (1956) Acidity of catalyst surfaces. I. Acid strength from colors of adsorbed indicators : *J. Amer. Chem. Soc.*, v. 78, pp. 5490–5494.

Brindley, G. W. and Youell, R. F. (1951) A chemical determination of the tetrahedral and octahedral aluminum ions in a silicate : *Acta Cryst.* v. 4, pp. 495–497.

Brunauer, S., Emmett, P. H. and Teller, E. (1938) Adsorption of gases in multimolecular layers : *J. Amer. Chem. Soc.* v. 60, pp. 309–319.

Grim, R. E. (1953) *Clay Mineralogy* : McGraw-Hill Book Company, Inc., New York, 384 pp.

Kerr, G. T., Zimmerman, R. H., Fox, H. A., Jr. and Wells, F. H. (1956) Degradation of hectorite by hydrogen ion : in *Clays and Clay Minerals*, Natl. Acad. Sci—Natl. Res. Council pub. 456, p. 322–329.

Lepper, H. A., Ed. (1945) *Official and Tentative Methods of Analysis* : Association of Official Agricultural Chemists, Washington, D.C., pp. 13–20.

Mathews, A. C., Weed, S. B. and Coleman, N. T. (1955) The effect of acid and heat treatment on montmorillonoids, in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council pub. 395, pp. 403–412.

Osthaus, B. (1954) Chemical determination of tetrahedral ions in nontronite and Montmorillonite, in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council pub. 327, pp. 404–417.

Osthaus, B. (1956) Kinetic studies on montmorillonites and nontronite by the acid-dissolution technique, in *Clays and Clay Minerals*, Natl. Acad. Sci.—Natl. Res. Council pub. 456, pp. 301–321.

Packter, A. (1955) Catalysis by complexing anions. The kinetics of the activation of montmorillonite clays : *Chem. & Ind. (Rev.)*, p. 1384.

Walling, C. (1950) The acid strength of surfaces : *J. Amer. Chem. Soc.*, v. 72, pp. 1164–1168.