

NaOH DISSOLUTION OF SOME OXIDE IMPURITIES FROM KAOLINS*

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ABSTRACT

A working definition for allophane includes amorphous silica and alumina that are quickly soluble in boiling $n/2$ NaOH. Kinetic studies are used to differentiate and to make a rough estimation of the amount of allophane and certain other impurities present in some kaolin minerals.

Solution rate studies on opal, gibbsite, two allophanes, volcanic ash, quartz, two halloysites, and two kaolinites are presented and in most cases the reaction rate orders with respect to the hydroxide treatment are determined. No interpretation of the observed rate orders are presented.

The decomposition of the two kaolinites followed a third order rate law and their rate constants varied approximately by a factor of ten. The decomposition of the two halloysites followed a second order rate law and their rate constants varied approximately by a factor of five. It is not known why specimens of the same mineral species from different localities should have such large variations in their dissolution rates. Differences in their degree of crystallinity and the resulting surface area may be responsible.

INTRODUCTION

AN amorphous material is one in which the particle size is either too small or the crystals are too disordered to sufficiently reinforce the diffracted X-rays, although short-range structural order certainly exists. Amorphous aluminosilicates in clays, soils, and sediments range from freshly coprecipitated aluminum and silicon oxides through mixed amorphous silica and alumina to layer silicate relics which have been leached of most cations other than silicon and aluminum (Ross and Kerr, 1934; Aomine and Jackson, 1959; Fields, 1955; Dyal, 1953). Volcanic glass, silica skeletal remains of secreting organisms, and opal are additional amorphous forms containing silica. According to Searle and Grimshaw (1959), opal is an amorphous hydrated form of silica with the composition

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$\text{SiO}_2 \cdot n\text{H}_2\text{O}$ where the percentage of water is usually less than 10. It is found in rocks of many kinds, but is of secondary origin behaving as a dried-up gel filling cracks and fissures and cementing grains of other minerals. Coprecipitated and individually precipitated oxides of silicon and aluminum are perhaps the more common forms. Allophane is the name which was originally given to a presumably coprecipitated, amorphous aluminosilicate lining the cavities in marl, but the term is now generally applied to all amorphous aluminosilicates. Aomine and Jackson (1959) have designated the coprecipitated type of allophane as "Ando type", while Fields (1955) has designated the coprecipitated type as allophane A and a mixture of amorphous forms of silica and alumina as allophane B. Allophane is used in the general sense in this paper as no attempt has been made to ascertain the specific type or types of allophane present.

The occurrence of allophane in clays, soils, and sediments has been reported with such increasing frequency in the last few years that, in a manner analogous to organic matter and iron oxides, some allophane should probably be considered to be present as an impurity unless shown to be absent. Thus, in the course of a study of the effect of impurities on the rheological behavior of kaolinites it was considered necessary to include allophane as a possible impurity. This investigation using boiling $N/2$ sodium hydroxide was therefore undertaken to determine: (1) the length of time necessary to extract allophane; (2) the solubility of some oxides of silicon and aluminum frequently found as impurities in clays; and (3) the solubility of kaolinite and halloysite.

EXPERIMENTAL PROCEDURES

The identification and source of the samples used in this study are given in Table 1. The quartz and gibbsite were portions of samples previously used for thermodynamic determinations by Barany and Kelley (1961).

The minerals were ground in a mullite mortar to pass a 325 mesh sieve. Kaolinite-2, kaolinite-7, and halloysite-29 were subjected to additional treatments. They were: (1) blended for 5 min in N NaOAc (pH 5.0) and passed through a 325 mesh sieve; (2) centrifuged, resuspended in N NaOAc and heated on a steam bath for 15 min; (3) retreated as in treatment (2); (4) centrifuged and the recovered clay was washed three times with N NaCl; (5) dialyzed until salt free; (6) dried at 60°C ; and (7) crushed to pass a 100 mesh sieve.

Alkali extractions were carried out using plastic or stainless steel containers and apparatus throughout. One hundred ml of $N/2$ NaOH in a 500 ml stainless steel beaker was brought to a boil using a plastic funnel inserted in the beaker as a reflux condenser. A stainless steel stirring paddle was passed through the funnel and attached to a variable speed stirrer. One hundred mg (approximately) of sample, unless otherwise

TABLE 1.—IDENTIFICATION OF MINERALS

Sample	Identification	Source
Allophane-56	—20 μ fraction of Japanese Volcanic Ash Soil	S. Aomine Kyushu University Fukuoka, Japan
Allophane-59	Lawrence County, Indiana	W. A. White, Illinois Geological Survey
Cristobalite-51b	Inyo County, California	Wards Natural Science Establishment
Gibbsite-51	See page 634	K. K. Kelley, U.S. Bureau of Mines, Berkeley, California
Halloysite-12	A.P.I. Halloysite No. 12b North Gardiner Mine Bedford, Indiana	Wards Natural Science Establishment
Halloysite-29	A.P.I. Halloysite No. 29 Wagon Wheel Gap, Colorado	Wards Natural Science Establishment
Kaolinite-2	A.P.I. Kaolinite No. 2 Birch Pit, Macon, Georgia	Wards Natural Science Establishment
Kaolinite-7	A.P.I. Kaolinite No. 7 Dixie Rubber Pit, Bath, S.C.	Wards Natural Science Establishment
Opal-51b	Virgin Valley Humboldt County, Nevada	Wards Natural Science Establishment
Quartz-51	See page 634	K. K. Kelley, U.S. Bureau of Mines, Berkeley, California
Volcanic Ash (VH ₁ -“FL-16”)	Hunt's Site	R. Van Horn U.S. Geological Survey Denver, Colorado

specified, was added and the extraction carried out for varying periods of time with the vapor loss being compensated for by periodic additions of water. At the appropriate time the beaker was removed and quenched with 50 ml (later in the study 150 ml) of distilled water and immediately immersed in a pan of cool tap water until the beaker could be picked up and swirled by hand without discomfort. A clear solution was then obtained by centrifugation and stored in a plastic bottle. An insufficient amount of either the extraction or quench liquor will cause reprecipitation (Foster, 1953; Hashimoto and Jackson, 1960).

TABLE 2.—WEIGHT PER CENT OF SILICA AND ALUMINA DISSOLVED BY BOILING N/2 NaOH FROM QUARTZ, OPAL, GIBBSITE, CRISTOBALITE, ALLOPHANE, AND VOLCANIC ASH SPECIMENS AS A FUNCTION OF TIME

Extraction time (min)	Quartz-51		Opal-51b		Gibbsite-51		Cristobalite-51b		Allophane-56		Allophane-59		VH ₁ —"FL-16" Volcanic Ash	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
½	0.026	—	—	62.9	1.35	0.26	—	—	—	—	—	—	—	—
1½	0.030	—	22.8	75.9	2.45	0.44	—	—	—	—	—	—	—	—
3	0.046	—	37.6	80.3	3.84	0.53	19.9	23.7	29.5	50.7	16.8	10.6	—	—
6	0.051	—	59.0	88.5	4.34	0.51	20.8	24.9	29.6	50.1	19.1	12.4	—	—
12	0.080	—	85.3	90.0	6.75	0.66	22.7	25.8	—	—	—	—	23.5	14.9
24	0.115	—	93.4	93.7	12.1	1.06	24.2	25.9	—	—	—	—	28.9	17.3
48	0.220	—	94.9	92.8	16.9	1.21	—	—	—	—	—	—	25.6	17.6
96	0.352	—	—	—	22.7	2.27	—	—	—	—	—	—	31.5	21.1

Total alumina and silica content of the kaolinite and halloysite specimens was determined by decomposing 50 to 75 mg of clay with 10 ml of 15 per cent NaOH in a platinum crucible, through evaporation, followed by heating to a dull red heat for 20 to 30 min and cooling with the solids being taken up in 20 ml of 1 : 1 HCl (overnight) and diluted to 1000 ml. Liquor analysis was then accomplished as indicated below.

Alumina was determined with alizarin red-S and silica with reduced molybdate (Shapiro and Brennack, 1956) using a Beckman DU spectrophotometer. Both aluminum and silicon were calculated as the oxide for purposes of calculating the per cent of the sample weight extracted. The moisture free weights were determined after firing at 815°C for 20 hr.

RESULTS AND DISCUSSION

The data for silica and alumina removed by the extraction process as a function of time for quartz-51, opal-51b, gibbsite-51, cristobalite-51b, allophane-56, allophane-59, and volcanic ash-VH₁-“FL-16”, can be found in Table 2, while Table 3 contains similar data for kaolinite-2,

TABLE 3.—WEIGHT PER CENT OF SILICA AND ALUMINA DISSOLVED BY BOILING N/2 NaOH FROM KAOLINITE AND HALLOYSITE SPECIMENS AS A FUNCTION OF TIME*

Time (min)	Kaolinite-2		Kaolinite-7		H alloysite-12		Halloysite-29	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
½	0.77	0.20	2.20	1.74	10.2	15.9	2.84	2.30
1½	0.69	0.13	2.49	2.28	14.8	22.2	5.32	3.50
3	0.40	0.47	4.78	3.81	21.9	29.5	10.0	8.63
6	1.43	0.81	8.68	7.36	30.4	36.1	15.3	13.0
12	2.13	1.30	14.7	12.7	34.7	42.4	21.2	18.0
24	4.06	2.61	23.1	18.6	39.1	47.2	28.0	24.1
48	6.85	4.83	28.1	22.2	40.6	48.8	35.9	29.4
96	11.1	8.13	33.0	26.3	—	—	41.7	36.3
Total available†	52.5	37.6	50.3	41.2	43.2	50.7	49.9	41.0

*On the basis of solids at 815°C.

†By NaOH fusion method (weight per cent).

kaolinite-7, halloysite-12, and halloysite-29. In addition, Table 4 contains evaluations for the per cent of the total available silica and alumina extracted from the kaolinite and halloysite specimens as a function of time based on total silica and alumina content as determined by the sodium hydroxide fusion method.

TABLE 4.—PER CENT OF TOTAL AVAILABLE SILICA OR ALUMINA DISSOLVED FROM THE KAOLINITE SPECIMENS AS A FUNCTION OF TIME.
(Calculated from Table 3)

Time (min)	Kaolinite-2		Kaolinite-7		Halloysite-12		Halloysite-29	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
½	1.47	0.53	4.38	4.22	23.6	31.4	5.70	5.60
1½	1.31	0.35	4.95	5.54	34.2	43.8	10.6	8.52
3	0.76	1.25	9.50	9.25	50.6	58.1	20.0	21.1
6	2.72	2.15	17.3	17.9	70.2	71.1	30.6	31.7
12	4.06	3.46	29.2	30.8	80.2	83.6	42.5	43.9
24	7.73	6.94	46.0	45.2	90.4	93.5	56.1	58.7
48	13.0	12.8	56.0	54.0	94.1	96.2	72.0	71.6
96	21.1	21.6	65.6	63.9	—	—	83.5	88.5

Analysis of the extraction rate data in terms of chemical kinetics was undertaken to evaluate its usefulness in the following aspects:

- (1) To determine the extraction time required to free a given 1 : 1 layer silicate from the more soluble components.
- (2) To estimate the amounts and types of alumina and/or silica impurities present.
- (3) To determine variations in the alkali solubility rate for different specimens of a given mineral species.

The rate of a reaction may be determined by measuring the amount of a reactant consumed, or of any product produced by the reaction, as a function of time. Such rates are usually measured per unit volume per

TABLE 5.—RATE LAWS.

Order	Differential Form*	Integrated Form*
Zero	$- dx/dt = k_0$	$x = x_0 - k_0 t$
First	$- dx/dt = k_1 x$	$\ln x = \ln x_0 - k_1 t$
Second	$- dx/dt = k_2 x^2$	$1/x = 1/x_0 + k_2 t$
Third	$- dx/dt = k_3 x^3$	$1/x^2 = 1/x_0^2 + 2k_3 t$

*Where: x_0 = original concentration (weight/volume)

x = amount of reactant not yet consumed at time t
(weight/volume)

t = time

k_n = specific rate constant, where n indicates the rate order.

unit time and the rate itself will be proportional to some function of the reactant concentration. The exponent of this concentration term in the different form of the rate law defines the order of the reaction. Some forms of the differential and integrated rate laws are given in Table 5 in which the constant k_n is the "specific rate" or "rate constant".

The determination of the reaction rate order governing the dissolution of various specimens was facilitated by preparation of a master set of graphs (Bray and Rollefson, 1954) wherein the per cent completion of a reaction was plotted as a function of $\frac{k_0}{x_0}t$, $k_1 t$, $k_2 x_0 t$ or $k_3 x_0^2 t$, respectively, for zero, first, second, and third order reactions (Fig. 1). Changes in the magnitude of the rate constant will only shift the curve of a given rate order reaction in a horizontal direction. By simply plotting the experi-

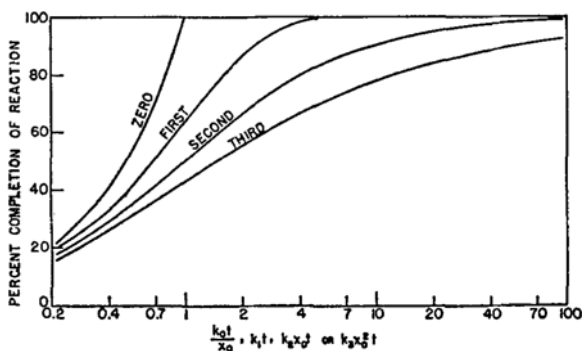


FIGURE 1.—Reaction rate order master graph.

mental data as per cent completion vs. time, one can determine the rate order and rate constant by comparing it with the master curves which are plotted on similar paper. This device is particularly useful when applied to an extraction curve representing the dissolution of complex systems. No particular rate law is then followed. At times, however, this method will identify the presence of small amounts of a phase with a faster solution rate than the main phase, or of some insoluble residual material. If desired, conventional plots of time vs. $f(x)$ can then be made to confirm the rate order and to calculate the rate constant.

Oxide Minerals

The solution rates of the oxides were determined to evaluate the error that might be introduced in the course of estimating the quality of allophane present from solubility data as well as to study the possibility of removing the free oxides of aluminum and silicon in order to purify kaolins.

As shown in Table 2 and Figs. 2a and 2b, the solution rate in $N/2$ NaOH for various oxides increases in the following order: quartz-51 < cristobalite-51b < opal-51b < gibbsite-51.

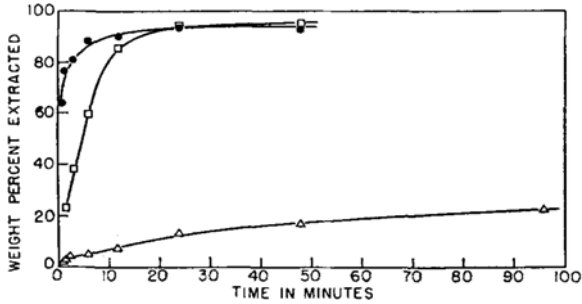


FIGURE 2a.— SiO_2 and Al_2O_3 extracted from some oxide minerals. The weight per cent silica dissolved from opal-51b and cristobalite-51b are represented by \square and Δ , respectively, while \bullet represents the weight per cent alumina dissolved from gibbsite-51.

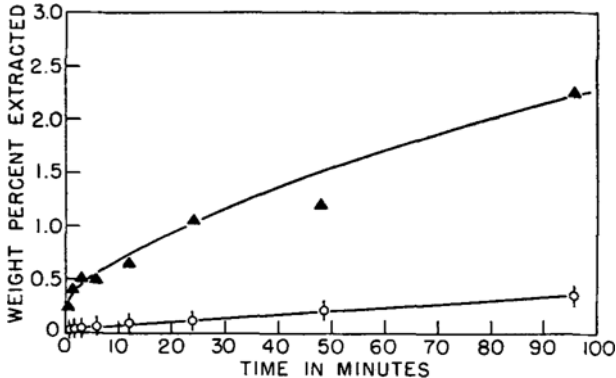


FIGURE 2b.— SiO_2 and Al_2O_3 extracted from some oxide minerals. The weight per cent silica dissolved from quartz-51b is represented by \circ , while \blacktriangle represents the weight per cent alumina dissolved from cristobalite-51b.

This data plotted on semilog paper are presented in Fig. 3. The open triangles represent the uncorrected solubility data for the dissolution of opal-51b. A curve through these points levels off at a value of 95 per cent which indicates that about 5 per cent of this specimen is either some other less soluble silicate or nonsilicate impurity. The closed triangles represent this data recalculated on the basis that only 95 per cent of the specimen

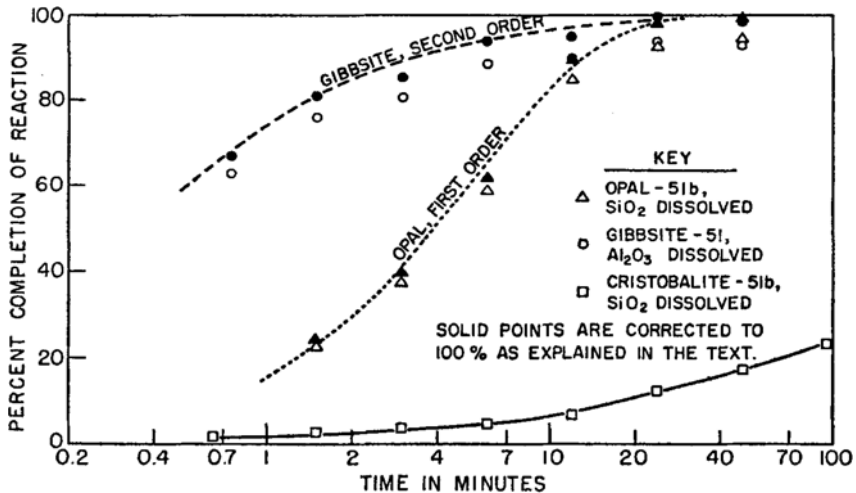


FIGURE 3.—Reaction rate order plot of opal, gibbsite, and cristobalite.

is available in the dissolution process as SiO_2 . The dotted line represents the path that a first order reaction would follow; thus the opal-51b dissolution in the boiling $N/2$ NaOH follows first order kinetics.

Also in Fig. 3, the open circles represent the solubility data for gibbsite-51, while the closed circles represent the data recalculated on the basis that only 94 per cent of the specimen is available as Al_2O_3 . The dashed line represents the path a second order reaction would follow and indicates the dissolution of gibbsite-51 in boiling $N/2$ NaOH follows a second order rate law.

The cristobalite-51b solubility data plotted in Fig. 3 probably indicate that at least two phases are present, or that there is a change in the kinetics after a 7 to 10 min induction period which would represent the time required for an intermediate step to reach steady state conditions. The overall solubility rate of this material is low and the reaction was not carried to a high enough degree of completion to establish its order of rate law. It is of interest to note that the alumina dissolved from this cristobalite is equal to approximately 10 per cent of the amount of silica dissolved, and that over the range of samples studied (up to 96 min extraction time) the ratio of alumina to silica extracted remained constant indicating that they were in a combined form.

The dissolution of quartz-51 under these conditions was very slow and no attempt was made to establish the rate order of its dissolution process in boiling $N/2$ NaOH.

It is apparent that both gibbsite and opal would be largely dissolved in the course of a 5 to 10 min extraction. However, because opal is an

amorphous oxide of silicon, it is properly included in our working definition of allophane. Because gibbsite is crystalline, it is undesirable for it to be included in the amorphous fraction. If present, its quantity should be estimated by other techniques and subtracted from the chemical analysis. Removal of quartz and cristobalite from kaolins by alkali extraction is not feasible.

Allophane and Volcanic Ash

The amounts of SiO_2 and Al_2O_3 removed from allophane-56, allophane-59, and volcanic ash by boiling $N/2$ NaOH as a function of time are shown in Fig. 4. Allophane-59 is almost instantly soluble and releases about 51 per cent Al_2O_3 and 30 per cent SiO_2 into a clear solution with no residual solids within 3 min. Allophane-56 releases 24 per cent Al_2O_3 and 20 per

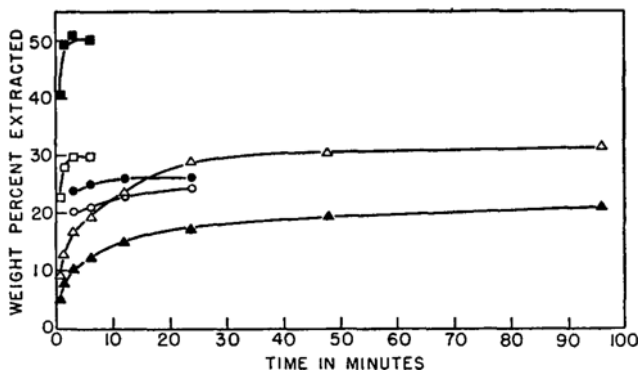


FIGURE 4.— SiO_2 and Al_2O_3 extracted from allophanes-56 and -59 and volcanic ash. The dissolution products from allophane-56, allophane-59, and volcanic ash VH_1 — “FL-16” are represented by circles, squares, and triangles, respectively. The solid points are Al_2O_3 and the open points SiO_2 .

cent SiO_2 in this same time period but some solids are still present. In addition, allophane-56, the less than 20 micron fraction from a Japanese volcanic ash soil, continues to dissolved with increasing time indicating that two different rate laws are being followed. Both of these allophane dissolutions (allophane-59 and allophane-56) appear to follow a first order rate law and the allophane contents are estimated as being 81 per cent for allophane-59 and 44 per cent for allophane-56.

The dissolution of the volcanic ash is much slower than that of the allophanes, although a portion of it (about 20 per cent) appears to have dissolved quite rapidly indicating that more than one phase is probably present.

Kaolins

Arithmetic plots of the per cent SiO_2 and Al_2O_3 extracted from the kaolinite and halloysite specimens as a function of time are presented in Figs. 5 and 6. This type of plot does not provide any specific clues as to the presence of impurity phases. However, by converting the solubility data to the per cent of the total available SiO_2 and Al_2O_3 extracted as indicated in Table 4, and plotting this data vs. the log of time so as to make reaction rate order plots as in Fig. 7, the following deductions can be made:

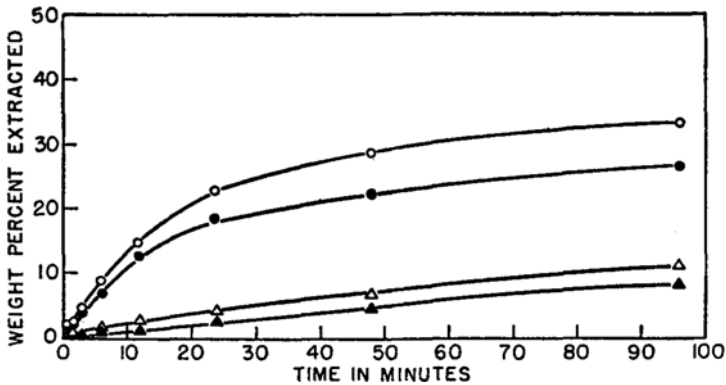


FIGURE 5.— SiO_2 and Al_2O_3 extracted from kaolinites-2 and -7. The dissolution products from kaolinite-2 (triangles) and kaolinite -7 (circles) are represented by open points for silica and by solid points for alumina.

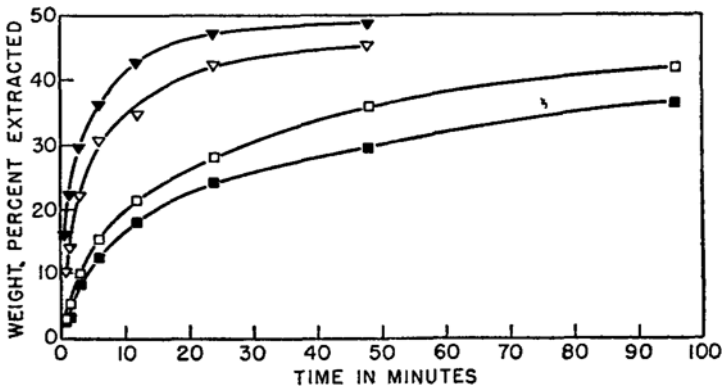


FIGURE 6.— SiO_2 and Al_2O_3 extracted from halloysites-12 and -29. The dissolution products from halloysite-12 (triangles) and halloysite-29 (squares) are represented by open points for silica and by solid points for alumina.

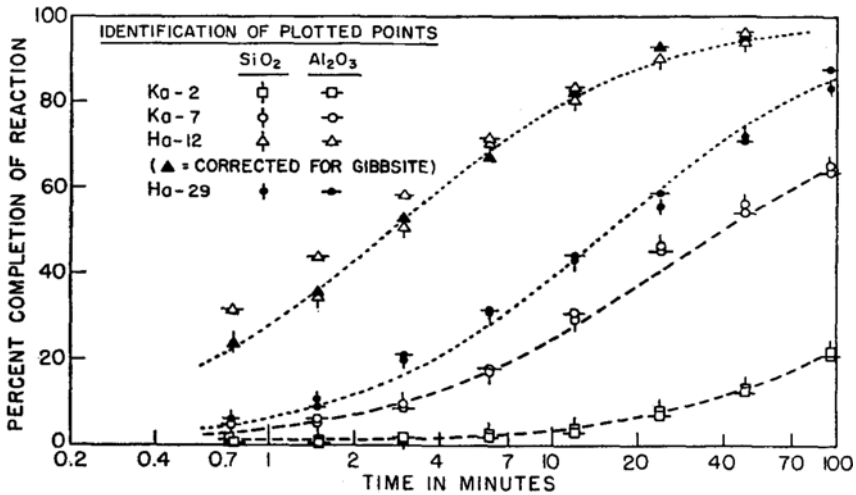


FIGURE 7.—Reaction rate order plots of kaolinites-2 and -7 and halloysites-12 and -29.

(1) The differential solution rates of both kaolinites follow a third order rate law with respect to the $n/2$ NaOH treatment in which the kaolinite-2 decomposition rate is much slower than that of kaolinite-7. Their rate constants (k_3) are approximately $0.0033 \text{ (mg/cc)}^{-2} \text{ (min)}^{-1}$, and $0.038 \text{ (mg/cc)}^{-2} \text{ (min)}^{-1}$. The dashed lines in Fig. 7 represent the path a theoretical third order rate law would follow. By noting the deviations found in the experimental points from these theoretical dashed lines for the shorter extraction periods, one can estimate on this basis that as much as 1 per cent of the total available SiO₂ in specimen kaolinite-2, and as much as 2 per cent of each of the total SiO₂ and Al₂O₃ contained in kaolinite-7 appears to be quickly soluble and might be classified as being allophane.

(2) The decomposition of both of the halloysites follow a second order rate law with respect to the $n/2$ NaOH treatment. Halloysite-29 with an approximate rate constant of $k_2 = 0.063 \text{ (mg/cc)}^{-1} \text{ (min)}^{-1}$ was much slower than halloysite-12 whose rate constant was approximately $k_2 = 0.30 \text{ (mg/cc)}^{-1} \text{ (min)}^{-1}$. For the case of halloysite-29, as much as 2 per cent of the total available SiO₂ and a similar amount of the Al₂O₃ were dissolved faster than predicted by the rate law and could be from a form that is more quickly soluble than halloysite-29 as indicated in Fig. 7. Halloysite-12 presents a more complicated problem. The open triangles in Fig. 7 show that the silica being removed is following the path of a second order reaction and that the Al₂O₃ dissolution does not appear to follow any rate law in particular. However, for this halloysite-12 specimen, on the basis of the chemical analysis as well as D.T.A. and X-ray evaluations, it was

estimated that 10 per cent gibbsite was present. The solution rate data of gibbsite-51 was used in correcting the data for the effect of this impurity. The remaining Al_2O_3 going into solution was then due to halloysite dissolution and is represented by the solid triangles which agree very well with the silica solution data. The solution rate of halloysite-12 itself was too fast to allow an estimation of the allophane content, if present. The dotted lines in Fig. 7 indicate the path a theoretical second order rate law dissolution follows.

Murray and Lyons (1956) describe poorly crystalline kaolinites as having X-ray diffraction peaks with broader peaks at half height, and the crystals as being thinner with larger surface areas. Such imperfections also cause the X-ray diffraction reflections involving the a and b cell dimensions to be poorly resolved. The X-ray pattern of specimen kaolinite-2 corresponds to their specimen "H" while specimen kaolinite-7 corresponds to their specimen "K" which they state is inferior in its degree of crystallinity. It is not known if the difference between the degree of crystallinity of these two specimens and the corresponding surfaces would be large enough to account for the observed differences in dissolution rate, or if some other difference in fundamental structure must be present. In a similar manner, halloysite-29 was observed to have a higher degree of crystallinity than halloysite-12. Since this work was directed only at the removal of oxide impurities, this point was not further pursued.

CONCLUSIONS

1. All of the common minerals present in clays, including kaolinite, halloysite, and allophane, were found to be soluble in varying degrees in boiling $N/2$ NaOH.

2. The dissolution of monomineralic-clay minerals in boiling $N/2$ NaOH generally follows a characteristic rate law for a given mineral. However, solution rate and solubility data by itself are not sufficient to identify a mineral because of large differences in the solution rates of different specimens of the same mineral species. It is necessary to also use X-ray, D.T.A., and possible other techniques. The determination of the dissolution mechanism causing adherence to a particular rate law and large variations in solution rate was not an objective of this study.

3. The solution rate data of the silica and alumina dissolved in boiling $N/2$ NaOH from samples consisting of more than one phase did not follow any particular rate law. A kinetic analysis of the solution rate data of a sample, however, may disclose information useful in assisting in the

determination of its mineralogical composition. At any particular time silica or alumina being taken into solution may originate from different sources. The presence of small amounts of a relatively slow or fast dissolving phase can be established by preparing kinetic plots of the "percent completion of a reaction" vs. the "log of time". By correcting such solution rate data for the presence of impurities, when the main phase is a clay mineral, the resulting data generally follows a rate law and represents a mono-mineral.

4. Rapid dissolution of silica or alumina from a sample in boiling $N/2$ NaOH does not necessarily indicate the presence of allophane. Poorly crystalline halloysite and kaolinite also exhibit rapid dissolution in boiling $N/2$ NaOH.

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