Reactions of Aqueous Aluminum Species at Mineral Surfaces

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By D. W. BROWN and J. D. HEM

CHEMISTRY OF ALUMINUM IN NATURAL WATER

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CHEMISTRY OF ALUMINUM IN NATURAL WATER

REACTIONS OF AQUEOUS ALUMINUM SPECIES AT MINERAL SURFACES

By D. W. BROWN and J. D. HEM

ABSTRACT

Aqueous aluminum solutions containing 4.5×10^{-4} molar aluminum in 0.01 molar $NaClO_4$ were partly neutralized with NaOH to give OH:Al mole ratios from 1.40 to 2.76. Measured amounts of montmorillonite, kaolinite, volcanic ash, or feldspathic sand were added to provide an area of inert surface. Reactions that occurred during 100 days of aging were compared with those in similar solutions without added surfaces, studied in earlier work.

Adsorption of monomeric species $Al(H_2O)_6^{+3}$, $AlOH(H_2O)_5^{+2}$, and $Al(OH)_2(H_2O)_4^{+}$ on the added surfaces follows a cation exchange mass law equilibrium model, and adsorption is essentially complete in 1 hour. Only minor changes in monomeric aluminum species occurred after that.

Rapid adsorption of polynuclear aluminum hydroxide species also occurs and follows the pattern of the Langmuir adsorption isotherm. In the absence of surfaces, the polynuclear ions slowly increase in size and become microcrystalline gibbsite during aging. Electron micrographs showed microcrystalline gibbsite was present on surfaces after aging only 2 days. However, the analytical data suggest this material must have been adsorbed after it had already attained a near-crystalline state. Adsorbed polynuclear aluminum hydroxide species were not extensively converted to microcrystalline gibbsite during 100 days of aging.

PURPOSE AND SCOPE

In an earlier paper in this series, Hem and Roberson (1967) dealt with the form and stability of aqueous aluminum hydroxide complexes at various ranges of pH. They reported that below neutral pH the dissolved aluminum species consist of three forms, (1) the monomeric octahedral $Al(H_2O)_6^{+3}$, $AlOH(H_2O)_5^{+2}$, $Al(OH)_2(H_2O)_4^{+}$, and $Al(OH)_4(H_2O)_2^{-}$ ions, (2) a positively charged polymeric species consisting of octahedral units held together by double hydroxide bridges and containing as much as several hundred aluminum atoms, and (3) hexagonal microcrystalline gibbsite particles with maximum diameters near $0.1 \mu m$ (micrometre). In a later report, Smith and Hem (1972) described the effect of aging on these species designated by them Al_a, Al_b, and Al_c, respectively. No clearly defined boundary exists between

Al_b and Al_c with regard to molecular size; the boundary used for convenience is an analytical one. When Al_a, Al_b, and Al_c are placed in contact with the complexing agent ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) under mildly acidic conditions, the Al_a reacts completely in less than 1 minute, and the Al_b reacts in a relatively slow first-order reaction having a half-time of 5–20 minutes. The Al_c form does not readily react with the ferron and is stable for several days in this environment.

Solutions were prepared by addition of differing amounts of hydroxide to solutions of Al^{+3}, so that they were supersaturated in Al_a with respect to gibbsite. The solutions approached equilibrium over several years aging as the polymeric Al_b species grew in size. This process lowered the pH, because the units lost hydrogen ions from some of the attached water molecules when hydroxide bridges were formed. The Al_a concentration remained relatively constant during aging; eventually the pH decreased to an equilibrium value. Between age times of 10–20 and 100–120 days, the disappearance of Al_b (to form Al_c) appeared to obey a first-order rate law.

The experimental aging-study solutions used by Smith and Hem (1972) constituted a relatively simple system in comparison to the aluminum hydroxide species occurring in ground or surface water systems. The aluminum hydroxide species were studied separately and apart from other complicating factors such as the effects on dissolved aluminum of dissolved silica, fluoride, sulfate, and organic ligands, and of various types of mineral surfaces. These factors are being considered in other papers of the series "Chemistry of Aluminum in Natural Water."

The purpose of this paper is to describe the effects of representative mineral surfaces on the behavior of dissolved and suspended aluminum hydroxide species, especially with regard to adsorption of dissolved aluminum species by the surfaces and their effect on the rate of polymerization of Al_b to Al_c.

The general approach used in this investigation was to duplicate some of the experimental solutions prepared by Smith and Hem (1972), but with various known quantities of relatively insoluble minerals added in order to provide solid surfaces. Comparison of the results with those obtained in the absence of such surfaces permits a quantitative evaluation of their effects on the chemical reactions of aluminum that occur in systems moderately supersaturated with respect to gibbsite.

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developing the presentation and are acknowledged with thanks. We also wish to thank C. J. Lind for furnishing all the electron micrographs used in the report.

EXPERIMENTAL PLAN AND METHODS

The work was begun by preparing a series of solutions containing the same total concentration of aluminum (4.53×10^{-4} molar) but different amounts of added base. These aging-study solutions were prepared by a technique identical to that described by Smith and Hem (1972). The OH:Al ratio (r_n) in the solutions as made up varied from 1.40 to 2.76. The four solutions prepared were designated D, F, G, and H and were closely comparable with similarly designated solutions studied by Smith and Hem.

Smith and Hem (1972) found that the rate of addition of base in preparation of the aging-study solutions had a marked effect on the amount of Al_b and Al_c initially formed. Al_b concentration was found to decrease and Al_c concentration increase when the rate of base addition increased. Al_a concentration was found to be independent of this rate. The slower rates of base addition thus yielded solutions with a higher pH and farther from equilibrium than those obtained by fast addition of base. In this set of experiments, base was added dropwise over a period of 90–120 minutes in order to start the solutions with as much Al_b and as little Al_c and as far from equilibrium as practicable.

Each 3,000 ml (millilitres) solution (D, F, G, and H) was divided into 12 aliquots of 250 ml each and placed in polyethylene bottles in which measured amounts of the various surfaces had been placed. Thus from solution D were formed the following 12 solutions:

Amount and type of surface	*Abbreviation*	*Added surface (m^2)*	*Surface per volume (m^2/l)*
No added surface (a)	D NASA	0.0	0.0
No added surface (b)	D NASB	.0	.0
0.010 g Wyoming bentonite	D 0.01WB	5.5	22
0.10 g Wyoming bentonite	D 0.1WB	55	220
0.20 g Wyoming bentonite	D 0.2WB	110	440
0.020 g volcanic ash	D 0.02VA	2.2	8.8
0.10 g volcanic ash	D 0.1VA	11	44
0.50 g volcanic ash	D 0.5VA	55	220
0.10 g kaolinite #17	D 0.1K	1.5	6.0
0.50 g kaolinite #17	D 0.5K	7.5	30
2.0 g kaolinite #17	D 2.0K	30	120
1.0 g Monterey sand	D 1.0MS	.5	2.0

Solutions F, G, and H were similarly apportioned.

Each of these 48 solutions was analyzed for aqueous Al_a and Al_b in the manner described by Smith and Hem (1972). The aliquots used for analysis were centrifuged at 2,000 *G*'s for 1 minute in order to remove particulate suspended material that might interfere with the spectrophotometric measurements. A modification of the ferron-orthophenanthroline analytical method for aluminum (Brown and others, 1970) was used in which the pH of sample aliquots was never allowed to go below 5.0. Under these conditions, Al_a reacts immediately with the ferron, while Al_b reacts by first-order kinetics with ferron as these polymer species are attacked and dismantled by the acid. The half-time of the reaction ranges from 5 to 20 minutes, probably depending on the characteristic sizes and shapes of the Al_b polymers encountered. In any event, the reaction is at least 95 percent completed after 90 minutes of analysis time. Al_c does not react at a significant rate at pH 5. At a given analysis time, the amount of ferron-aluminum complex formation is determined spectrophotometrically at 370 nanometres. The concentration of Al_b present at zero analysis time is determined by extrapolation of the first-order reaction rate to zero time using a plot of analysis time versus the negative logarithm of aluminum concentration recovered. The intercept is the negative logarithm of the analyzed Al_b concentration (pAl_b). Al_a concentration is found by subtracting Al_b concentration from the total concentration recovered after 90 minutes. The remainder of aluminum not recovered is aqueous and adsorbed Al_c and also adsorbed Al_a and Al_b. At the same time as the aliquots for aluminum determinations were withdrawn, pH measurements were made using a Corning model 12 pH meter,[1] accurate to ±0.01 pH unit.

These Al_a, Al_b, and pH measurements were repeated at intervals of 1–3 days during the first 20 days of aging and at 5–15 day intervals after that. After the final analysis near the 100th day, dissolved silica concentrations were determined for each solution in order to evaluate the extent to which the added mineral surfaces might have undergone chemical attack and released solutes that influenced the processes of aluminum hydroxide polymerization.

CHARACTERIZATION OF SURFACES

The mineral materials used were selected to represent commonly occurring types similar to those that might be associated with natural water but more specifically definable than most natural soil or sediment. Two clays, kaolinite and montmorillonite, were used, and coarser grained material included volcanic ash and a feldspathic sand. The solids and their pretreatment are described subsequently.

The Wyoming bentonite (WB) was from a sample collected in January 1965 at Belle Fourche, S. Dak. It was dried at 90°C for 10

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[1] Use of trade names or commercial products in this report is for identification only and does not constitute endorsement by the U.S. Geological Survey.

minutes, then roller crushed to particle sizes of <200 mesh. Dry sieve analysis was 90 percent <20μm, while wet analysis showed 99 percent <20μm and 92 percent <0.5μm.

Ward's standard volcanic ash (New Mexico) fragments (VA) were ground in a mortar and pestle until all particles could pass through a 32-mesh sieve, were thrice washed in distilled water, and then dried at 90°C. Dry sieve analysis showed 100 percent <500μm, 67 percent <250μm, 48 percent <150μm, 42 percent <125μm, 35 percent <105μm, 19 percent <74μm, and 12 percent <44μm. Microscopic examination showed most of the particles to have irregular jagged surfaces to which no simple geometric model for evaluating surface areas could be applied.

Ward's standard kaolinite #17 (Lewistown, Montana) (K) was treated by the same method as that used on volcanic ash. No sieve analysis was performed.

Monterey sand, a beach sand from Monterey, Calif. (MS), was obtained from the Braun-Knecht-Heimann Company, San Francisco, Calif. It was twice washed with 35 percent Na_2SO_3 solution at pH 3 in order to remove MnO_2 formed on the sand surface in previous experimental studies by Hem (1964), who reported 55 percent of the grains were feldspar and 45 percent quartz. The grains were moderately rounded, and 85 percent of them were between 0.25 and 0.8 mm (millimetre) in diameter. None were larger than 0.8 or smaller than 0.1 mm.

The specific areas of the surfaces used were determined by the orthophenanthroline and ethylene glycol monolayer adsorption methods by Lawrie (1961) and Bower and Goertzen (1959), respectively. The orthophenanthroline adsorbed by a known amount of solid was determined by subtracting the concentration remaining in a solution shaken with the solid from the concentration of the saturated orthophenanthroline solution used. Analyses were made colorimetrically using the iron (II) orthophenanthroline complex. Specific surface areas obtained by this method are as follows:

Wyoming bentonite	550±40 m^2/g (metres squared per gram)
Volcanic ash	110±10 m^2/g
Kaolinite #17	15±2 m^2/g
Monterey sand	0.5±0.05 m^2/g

Ethylene glycol adsorbed by a known amount of solid was determined gravimetrically. Values obtained using this method are as follows:

Wyoming bentonite	550±110 m^2/g
Volcanic ash	118±10 m^2/g
Kaolinite #17	17±2 m^2/g

Cation exchange capacities of the surfaces used were determined using the method of Chapman (1965). By this procedure the clay or soil is saturated with sodium acetate, then ammonium acetate is used to replace the sodium which is then analyzed by atomic absorption spectrophotometry. Values obtained are as follows:

Wyoming bentonite	922 μeq/g (microequivalents per gram)
Volcanic ash	264 μeq/g
Kaolinite #17	69 μeq/g
Monterey sand	6.6 μeq/g

Determinations of the point of zero charge were made by measuring adsorption of hydrogen or hydroxide using the titration method described by T. W. Healy (oral commun., 1970), and the results obtained are as follows:

Wyoming bentonite	pH 8.1
Volcanic ash	8.4
Kaolinite #17	4.3

Cation exchange capacity for the four materials studied is closely related to surface area, as shown by the plot of these data (fig. 1). The degree to which this relationship may be more generally applicable is uncertain, however. For one thing, the two properties, exchange capacity and surface area, were measured by chemically similar techniques. The results thus have an internal bias that might lead to a relationship of this type. However, the wet adsorption procedures for surface area gave results that were in approximate agreement with a few measurements on the same materials made by the Brunauer-Emmett-Teller (BET) procedure. The surfaces of all four materials are similar in the sense that all are dominated by oxygen ions bonded to silicon, and some similarity in behavior should not be surprising. Surfaces with radically different structure would perhaps behave differently from the ones studied.

Electron micrographs of the Wyoming bentonite, volcanic ash, and kaolinite materials used in this study are given as figures 2–4. The thin plates of montmorillonite are well displayed in the bentonite. The volcanic ash is composed of irregular glassy shards without a well-defined crystal structure. The kaolinite consists mainly of rather large layered plates with the angular outline typical of this mineral.

LONG-TERM AGING EFFECTS

The solutions studied by Smith and Hem (1972) were analyzed at intervals over about 9 months, and their paper also included some data on equivalent solutions aged as much as 3 years. Most of the changes

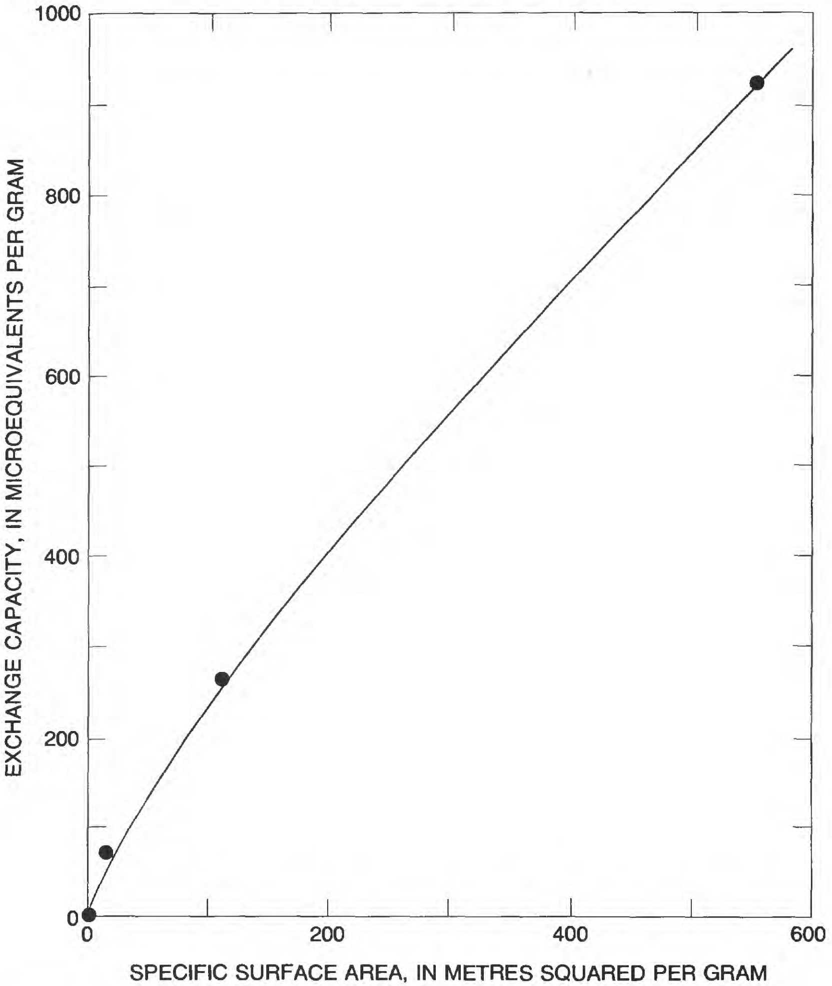

FIGURE 1.—Relation between specific surface area and cation exchange capacity for materials studied.

occurred in the first 4 months of study, however, and it therefore appeared possible to evaluate adequately the influence of the surfaces on the attainment of equilibrium solubility of aluminum with a maximum of 4 months of aging of the test solutions. The results of these experiments and factors considered in their interpretation follow. Observed pH and concentrations of aluminum species for each solution are given in tables 1–4.

INTERPRETATION OF RESULTS

The concentrations of dissolved species that can be measured, Al_a,

FIGURE 2.—Electron micrograph of Wyoming bentonite.

Al_b, and H^+, constitute the information that is available about the processes that occurred. Where correlated with what is known about the mineral surfaces, some insight into the nature of the processes ought to be possible. Several alternative hypotheses can be suggested as a starting point for the interpretation of the experimental data. The following are possible conditions and ways for evaluating them.

1. Chemical reactions may have occurred in which the surfaces were actually attacked and partly brought into solution. Such reactions might have produced a new solid aluminosilicate whose behavior would affect aluminum solubility in a way different from simpler aluminum hydroxide species. The extent of attack on the surfaces can be evaluated by determining dissolved silica in the aged solutions. A comparison of the halloysite ion activity products calculated from $Si(OH)_4{}^0$, Al^{+3}, and H^+ activities in these solutions with those observed by Hem, Roberson, Lind, and Polzer (1973) for such material should indicate the importance of

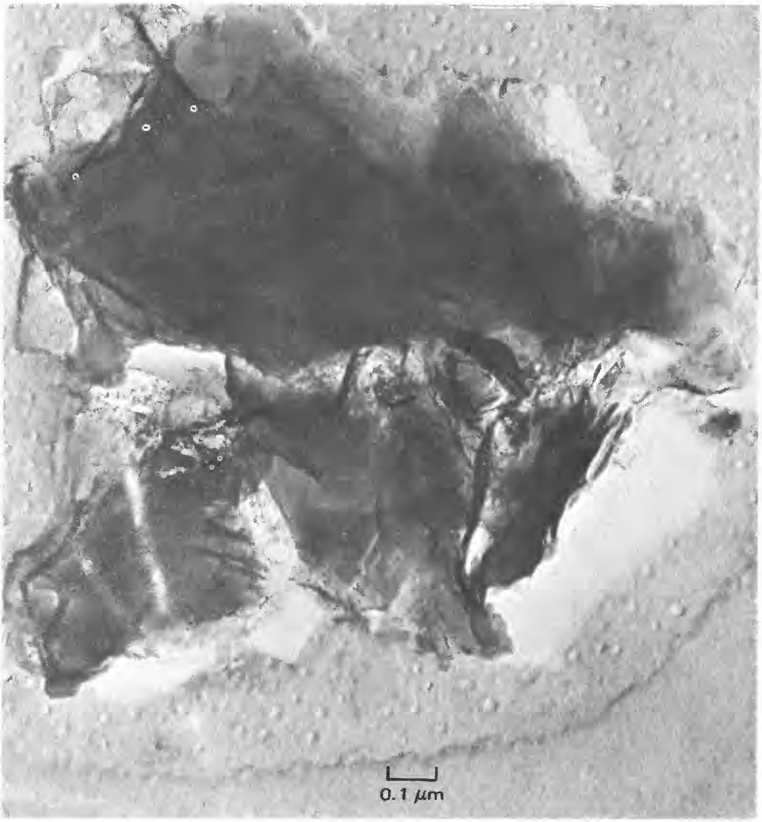

FIGURE 3.—Electron micrograph of volcanic ash.

reactions involving surface dissolution. If some of the solutions appear to be producing an aluminosilicate solid they should not be included in an evaluation of equilibria involving gibbsite.

2. Mineral surfaces catalyze or facilitate the processes of polymerization of aluminum hydroxide previously observed. Essentially this involves the conversion of Al_b to Al_c (gibbsite). It should be feasible to evaluate this possibility by comparing rates of dissappearance of Al_b and testing for adherence to gibbsite solubility equilibria or by observing the rate and extent of pH shift in the presence or absence of surfaces.
3. Mineral surfaces alter concentrations of cations in solution by chemisorption. This can be studied by applying cation exchange equilibria.
4. Physical adsorption of polymerized species of low surface charge density occurs. The behavior of Al_b and Al_c might be so affected and can be explored by surface adsorption models.

FIGURE 4.—Electron micrograph of kaolinite.

A combination of certain of these processes may well occur. From a systematic examination of the experimental data, however, it should be possible to decide which processes predominate. In addition to the chemical data, electron micrographs of solids before and after exposure to aluminum solutions are available. These provide qualitative evidence of crystallization processes at the surfaces.

POSSIBILITY OF ALUMINOSILICATE FORMATION

As pointed out earlier, if the mineral surface in a particular solution were attacked and partly dissolved, this could be detected by the presence of aqueous silica. Studies by Hem, Roberson, Lind, and Polzer (1973, p. 16) indicate that solutions containing aluminum in concentrations similar to the ones studied here, with 2.0 mg/1 (milligrams per litre) SiO_2 or less, precipitated only crystalline $Al(OH)_3$. Where more silica was present, there was a mixed product;

TABLE 1.—*Concentrations of two types of dissolved aluminum and pH in relation to age and amount and type of mineral surface in solutions D*

[Asterisks indicate solutions which attacked surfaces]

Age (days)	NAS A	NAS B	0.01WB	0.1WB	0.2WB	0.02VA	0.1VA	0.5VA*	0.1K	0.5K*	2.0K*	1.0MS
						Moles Al_a/litre $\times 10^4$						
4	1.90	2.09	1.73	1.08	1.96	1.89	1.96	1.82	1.06	0.05	1.72	1.95
8	2.02	2.21	1.96	1.22	.22	2.03	1.92	1.03	2.01	2.02	1.82	2.07
18	2.08	2.15	1.90	1.13	.21	1.97	1.92	.90	1.99	1.96	1.74	2.12
34	2.14	1.95	1.94	1.07	.09	2.10	1.96	.68	2.09	2.12	1.66	2.00
50	2.02	2.03	1.93	1.05	----	2.06	1.98	.82	1.98	1.93	1.46	1.91
69	1.92	1.89	1.86	1.07	----	1.92	1.82	.84	1.89	1.84	1.51	1.79
103	1.99	1.93	1.88	1.04	----	1.91	1.95	.94	1.80	1.76	1.44	1.67
						Moles Al_b/litre $\times 10^4$						
4	2.04	2.19	1.12	0.12	1.78	1.91	1.20	1.29	0.19	0.07	0.28	2.09
8	2.00	2.04	1.12	.11	.00	1.74	.78	.07	1.66	1.05	.32	2.04
18	1.95	2.00	.95	.07	.00	1.74	.62	.10	1.51	.85	.28	1.95
34	2.00	1.95	.85	.08	.00	1.58	.48	.06	1.55	.56	.22	1.95
50	1.78	1.82	.72	.10	----	1.48	.32	.04	1.38	.62	.41	1.82
69	1.91	1.66	.79	.09	----	1.55	.41	.05	1.38	.65	.34	1.91
103	1.91	1.41	.71	.13	----	1.51	.48	.02	1.38	.68	.42	2.00
						pH						
0	4.34	4.54	4.49	4.43	4.72	4.54	4.55	4.39	4.54	4.32	4.29	4.58
4	4.30	4.52	4.38	4.46	4.87	4.53	4.47	4.70	4.52	4.37	4.35	4.54
8	4.41	4.49	4.41	4.44	4.86	4.47	4.42	4.40	4.49	4.40	4.35	4.51
18	4.43	4.54	4.44	4.46	4.90	4.51	4.45	4.42	4.50	4.41	4.35	4.54
34	----	----	----	----	----	----	----	----	----	----	----	----
50	4.42	4.45	4.42	4.45	----	4.50	4.45	4.38	4.44	4.42	4.32	4.51
69	4.44	4.43	4.42	4.46	----	4.51	4.45	4.43	4.47	4.45	4.33	4.53
103	4.27	4.36	4.38	4.44	----	4.45	4.41	4.38	4.40	4.40	4.30	4.47

TABLE 2.—*Concentrations of two types of dissolved aluminum and pH in relation to age and amount and type of mineral surface in solutions F*

[Asterisks indicate solutions which attacked surfaces]

Age (days)	NAS A	NAS B	0.01WB	0.1WB*	0.2WB*	0.02VA	0.1VA	0.5VA	0.1K	0.5K*	2.0K*	1.0MS
						Moles Al_a/litre $\times 10^4$						
2	1.25	0.95	1.49	0.00	0.09	0.97	0.84	0.50	1.07	1.61	1.44	0.93
3	.85	.86	.92	.22	.07	.82	.69	.25	1.13	1.50	1.29	.66
6	.95	.92	.99	.27	.00	1.04	.97	.00	1.07	1.00	.66	.91
12	.97	.97	.90	.16	.35	.98	.98	.16	.98	.99	.76	.92
19	1.02	.97	.88	.19	.02	.20	.85	.12	.83	.95	.82	.85
32	.88	1.16	1.06	.18	.25	.98	.95	.11	.91	.98	.79	.93
45	.95	1.06	.95	.20	.04	.96	.90	.07	1.01	.94	.80	.93
69	1.18	1.20	1.16	.20	.24	1.27	1.18	.19	1.17	1.11	.86	1.25
82	1.00	----	1.09	----	----	1.00	.88	----	1.08	.88	.63	.97
98	1.21	----	1.14	----	----	1.25	1.06	----	1.26	1.13	.80	1.19
						Moles Al_b/litre $\times 10^4$						
2	3.02	2.88	2.14	0.43	0.06	2.51	1.66	1.38	2.45	1.58	0.21	2.75
3	2.88	2.95	2.29	.04	.03	2.69	1.70	.04	2.63	1.70	.15	2.88
6	2.75	2.81	2.09	.00	.02	2.57	1.48	1.15	2.45	1.45	.21	2.69
12	2.57	2.57	1.82	.02	.10	2.34	1.35	.05	2.19	1.26	.10	2.51
19	2.19	2.14	1.74	.05	.07	1.45	1.20	.04	2.14	1.29	.10	2.23
32	1.66	1.58	1.29	.02	.02	1.29	.85	.02	1.51	1.00	.06	1.58
45	1.17	1.05	1.05	.00	.00	.85	.56	.01	1.17	.93	.03	1.10
69	.59	.49	.51	.00	.00	.25	.09	.02	.60	.71	.04	.58
82	.38	----	.35	----	----	.16	.08	----	.37	.62	.07	.38
98	.32	.22	----	----	----	.10	.10	----	.26	.52	.04	.24
						pH						
0	4.75	4.75	4.74	4.69	5.33	4.75	4.75	4.68	4.76	4.70	4.53	4.76
2	4.65	4.65	4.65	4.73	5.36	4.69	4.68	4.74	4.67	4.65	4.55	4.72
3	4.64	4.48	4.64	4.70	5.39	4.65	4.64	4.74	4.66	4.63	4.54	4.67
6	4.56	4.59	4.62	4.67	5.38	4.60	4.61	4.80	4.63	4.62	4.55	4.67
12	4.57	4.57	4.58	4.78	5.53	4.59	4.58	4.79	4.61	4.60	4.51	4.60
19	4.48	4.48	4.48	4.66	5.27	4.28	4.52	4.76	4.60	4.63	4.63	4.48
32	4.03	4.29	4.47	4.72	5.41	4.43	4.49	4.76	4.48	4.52	4.47	4.43
45	4.38	4.38	4.45	4.75	5.36	4.42	4.46	4.68	4.44	4.53	4.45	4.40
69	4.04	4.25	4.38	4.72	5.35	4.33	4.41	4.85	4.41	4.54	4.45	4.36
82	4.25	----	4.38	----	----	4.31	4.38	----	4.40	4.52	4.43	4.34
98	4.29	4.40	----	----	----	4.30	4.31	----	4.38	4.54	4.48	4.35

TABLE 3—*Concentrations of two types of dissolved aluminum and pH in relation to age and amount and type of mineral surface in solutions G*

[Asterisks indicate solutions which attacked surfaces]

Age (days)	NAS A	NAS B	0.01WB	0.1WB*	0.2WB*	0.02VA	0.1VA	0.5VA	0.1K	0.5K*	2.0K*	1.0MS
Moles Al_a/litre $\times 10^4$												
1	0.24	0.23	0.17	0.02	0.00	0.18	0.19	0.00	0.21	0.29	0.31	0.30
3	.15	.19	.20	.04	.00	.13	.15	.00	.17	.29	.33	.24
7	.13	.17	.14	.02	.05	.20	.21	.00	.18	.29	.23	.21
14	.24	.32	.22	.08	.08	.24	.32	.00	.32	.33	.32	.25
25	.31	.34	.31	.04	.08	.34	.33	.00	.34	.31	.25	.30
51	.54	.74	.49	.09	.18	.63	.46	.07	.53	.50	.27	.45
64	.55	.60	.42	----	----	.57	.48	.00	.53	.38	---	.49
85	.59	.58	.51	----	----	.78	.55	.00	.59	.40	----	60
95	.70	.98	.57	----	----	.61	----	----	.66	.52	---	.43
Moles Al_b/litre $\times 10^4$												
1	2.88	2.88	2.19	0.01	0.04	2.63	1.91	0.15	2.63	1.95	0.41	2.75
3	2.81	2.75	2.14	.01	.01	2.63	1.70	.02	2.51	1.78	.19	2.69
7	2.69	2.63	2.09	.00	.00	2.40	1.35	.00	2.40	1.66	.06	2.51
14	2.29	2 40	1.86	.01	.03	2.19	1.15	.00	2.23	1.48	.02	2.34
25	1.74	1 74	1.51	.01	.00	1.51	.85	.00	1.74	1.29	.00	1.74
51	.83	.83	.74	.00	.02	.62	.21	.01	.89	.93	.01	.85
64	.56	56	.50	----	----	.38	.01	.01	.63	.79	----	.59
85	.32	.30	.23	----	----	.14	.00	.00	.37	.74	----	.34
95	.20	.22	.17	----	----	.13	----	----	.23	.62	----	.30
pH												
0	4.92	4.95	4.94	5.84	6.40	4.96	4.96	5.08	4.95	4.89	4.82	4.96
1	4.74	4.83	4.82	6.29	6.69	4.97	5.00	5.38	4.93	4.72	4.80	4.91
3	4.81	4.91	4.93	6.25	6.76	4.86	4.90	5.41	4.91	4.65	4.74	4.87
7	4.66	4.79	4.84	6.3	6.73	4.72	4.86	5.48	4.86	4.83	4.77	4.86
14	4.61	4.68	4.76	6.49	6.92	4.60	4.76	5.55	4.78	4.78	4.73	4.69
25	4.53	4.58	4.65	6.35	6.35	4.61	4.68	5.40	4.70	4.73	4.69	4.68
51	4.34	4.47	4.56	5.97	6.65	4.51	4.59	5.59	4.58	4.70	4.70	4.51
64	4.40	4.49	4.59	----	----	4.50	4.60	5.75	4.57	4.74	--	4.53
85	4.41	4.42	4.58	----	----	4.44	4.55	5.64	4.52	4.72	----	4.48
95	4.46	4.43	4.53	----	----	4.42	----	----	4.48	4.67	----	4.46

however, silica concentrations as much as 9.0 mg/l SiO_2 still gave solids that contained gibbsite identifiable by X-ray diffraction, and solubility data indicated a gibbsite equilibrium was reached. These observations suggest that if concentrations of SiO_2 remained below 9.0 mg/l, gibbsite would be precipitated in solutions similar to the ones prepared here. Nonetheless, it is expedient to examine aluminosilicate equilibria in all the solutions where silica was detected even if the amount is less than 9.0 mg/l, because higher levels might have been present in some of these systems at some time during the aging process.

To say whether a solution may be at equilibrium with respect to a silicate, we must first determine from the H^+, Na^+, Al^{+3}, and $Si(OH)_4$ activities whether various solutions are saturated or supersaturated with respect to possible aluminosilicates. It can be shown that within the ranges of these activities in our solutions the most likely minerals for which saturation or supersaturation would occur are halloysite and kaolinite, for which the equilibrium can be written

$$\tfrac{1}{2}\, Al_2Si_2O_5(OH)_4 + 3H^+ \rightleftharpoons Al^{+3} + Si(OH)_4 + \tfrac{1}{2}\, H_2O$$

and

TABLE 4.—*Concentrations of two types of dissolved aluminum and pH in relation to age and amount and type of mineral surface in solutions H*

[Asterisks indicate solutions which attacked surfaces]

Age (days)	NAS A	NAS B	0.01WB	0.1WB*	0.2WB*	0.02VA	0.1VA	0.5VA*	0.1K	0.5K	2.0K*	1.0MS
						Moles Al_a/litre $\times 10^4$						
1	0.11	0.12	0.15	0.00	0.03	0.00	0.08	0.02	0.08	0.48	1.21	0.09
3	.02	.12	.21	.31	.12	.09	.06	.10	.52	.14	.00	.05
6	.00	.00	.00	.09	.31	.01	.00	.00	.02	.47	.00	.00
12	.09	.08	.08	.04	.00	.08	.12	.00	.12	.14	.04	.13
20	.22	.23	.02	.00	.00	.17	.13	.00	.19	.06	.02	.26
32	.19	.31	.16	.00	.03	.19	.22	.00	.22	.15	.02	.21
45	.25	.33	.17	.10	.18	.32	.08	.00	.20	.19	.11	.27
72	.46	.54	.27	.11	.23	.49	.27	.09	.32	.27	.05	.44
81	.27	.37	.21	----	----	.44	----	----	.26	.22	----	.34
97	.48	.42	.34	----	----	.46	----	----	.31	.30	----	.40
						Moles Al_b/litre $\times 10^4$						
1	2.57	2.57	1.95	0.20	0.05	2.34	1.58	0.23	2.40	1.74	0 34	2.51
3	2.57	2.57	2.04	.19	.19	2.23	1.29	.17	2.34	1.41	.08	2.45
6	2.57	2.51	2.04	.01	.01	2.14	1.02	.05	2.29	1.74	.58	2.40
12	2.09	2.14	1.41	.05	.03	1.82	.78	.07	1.86	1.23	.05	1.91
20	1.51	1.66	1.23	.02	.03	1.26	.39	.10	1.45	1.05	.02	1.41
32	1.05	1.15	.89	.08	.02	.85	.12	.02	1.50	.87	.03	.98
45	.71	.78	.55	.02	.01	.55	.04	.03	.74	.71	.01	.66
72	.31	.38	.19	.01	.14	.19	.10	.02	.32	.50	.02	.30
81	.24	.23	.10	----	----	.11	----	----	.32	.40	----	.19
97	.12	.14	.02	----	----	.03	----	----	.19	.33	----	.13
						pH						
0	5.10	5.12	5.13	6.33	6.89	5.18	5.18	5.50	5.14	5.07	5 12	5.16
1	5.19	5.31	5.39	6.59	6.53	5.33	5.45	6.09	5.40	5.25	5 19	5.36
3	5.01	5.17	5.30	6.59	7.01	5.22	5.34	5.92	5.22	5.32	5 20	5.21
6	5.06	5.08	5.10	6.45	6.45	5.18	5.22	5.90	5.18	5.12	5 09	5.17
12	4.45	4.78	5.01	6.44	7.00	5.00	5.02	5.87	5.07	5.07	5 03	4.88
20	4.40	4.50	4.83	6.63	7.03	4.75	4.93	5.75	4.87	4.99	5 01	4.82
32	4.59	4.68	4.73	6.56	6.96	4.72	4.75	5.82	4.82	4.93	4.97	4.67
45	4.54	4.63	4.68	6.45	6.85	4.64	4.70	5.93	4.70	4,87	4.97	4.66
72	4.47	4.55	4.66	6.40	6.9	4.63	4.66	5.95	4.66	4.87	5 15	4.58
81	4.51	4.53	4.59	----	----	4.53	----	----	4.61	4.85	----	4.55
97	4.46	4.55	4.64	----	----	4.52	----	----	4.64	4.87	----	4.61

$$\frac{[Al^{+3}]\,[Si(OH)_4]}{[H^+]^3} = K.$$

From the following thermodynamic data, it is possible to evaluate this equilibrium constant for three forms of clay, ranging from relatively unstable synthetic halloysite to well-crystallized kaolinite.

Species	ΔG°_f *(kcal/mole)*	*Reference*
Al^{+3}	−115.0	Latimer (1952).
$Si(OH)_4$	−312.7	Polzer and Hem (1965).
H_2O	−56.69	Latimer (1952).
$Al_2Si_2O_5(OH)_4$:halloysite	−898.4	Robie and Waldbaum (1968).
Synthetic halloysite	−897±1.0	Hem, Roberson, Lind, and Polzer (1973).
$Al_2Si_2O_5(OH)_4$:kaolinite	−902.87	Robie and Waldbaum (1968).

Mineral	$\Delta G_{reaction}$ *(kcal/mole)*	*K at 25°C for* $\frac{[Al^{+3}]\,[Si(OH)_4]}{[H^+]^3}$
Halloysite	−6.84	$10^{5.01}$
Synthetic halloysite	−7.54	$10^{5.53}$
Kaolinite	−4.61	$10^{3.38}$

The following relation can be used to calculate the thermodynamic activity of Al^{+3} in solutions of 0.01 ionic strength when pH and total Al_a are known:

$$[Al^{+3}]=\frac{(Al_a)}{2.34+\frac{1.47\times10^{-5}}{[H^+]}+\frac{1.91\times10^{-10}}{[H^+]^2}+\frac{7.6\times10^{-23}}{[H^+]^4}}.$$

The quantity (Al_a) is the analytically determined value in moles per litre. Calculated values for $[Al^{+3}]$ after approximately 100 days of aging are given in table 5. The activities of silicic acid ($Si(OH)_4$) in table 5 were calculated from the determined silica, assuming that this uncharged species has an activity coefficient of unity. The activity of OH^- was calculated from the measured pH, using $10^{-14.00}$ as the ion activity product for water.

The data in table 5 all represent the analysis made at the maximum aging time that gave useful information for calculating equilibrium solubility. Generally this was near 100 days. For some of the solutions, however, especially those having the larger amounts of silica, the concentration of Al_a dropped below the detection limit before that time. For these solutions a somewhat shorter aging period was used, for which a specific value for Al_a was available. The cation exchange capacity values in table 5 represent concentrations in equivalents per litre, calculated from the weights of solids added and their measured cation exchange capacity per unit weight.

From inspection of the plot of $pAl + pSi(OH)_4$ versus pH (fig. 5), it is apparent that several solutions from each group are supersaturated or near saturation with respect to synthetic halloysite. Generally those solutions containing 0.1 and 0.2 g Wyoming bentonite and 0.5 and 2.0 g kaolinite are those whose aluminum solubility may be controlled by silicate equilibria. The aluminum concentrations in these solutions may therefore be controlled by precipitation of aluminosilicate, although it is not possible to verify the existence of this kind of solid material in the presence of the added mineral material. A few of the solutions contained more than the 9 mg/l SiO_2 specified by Hem, Roberson, Lind, and Polzer (1973) as the upper limit for dissolved silica in solutions in which microcrystalline gibbsite was ultimately identified. It appears reasonable and proper to leave data from these solutions out of consideration in evaluating the behavior of aluminum in systems where dissolved silica is absent. It has been noted that Wyoming bentonite and volcanic ash, both having been found to have high points of zero charge (8.1 and 8.4, respectively), could have increased the pH by direct sorption of H^+. Kaolinite, having a low

TABLE 5.—*Aluminosilicate and gibbsite ion activity products and related data for solutions D, F, G, and H after 2–3* months aging

Solution	pH	(Al_a) (moles/l × 10^4)	SiO_2 (mg/l)	p[Al+3]	pSi$(OH)_4$	pOH	p[Al] [Si$(OH)_4$]	p[Al] [Si$(OH_4$] [H]−3	p[Al] $[OH]^3$	cation exchange capacity (equivalents/l × 10^4)
1 D NASA	4.27	1.99	0.0	4.13	----	9.73	----	----	33.32	---
2 D NASB	4.36	1.93	.0	4.16	----	9.64	----	----	33.08	----
3 D 0.01WB	4.38	1.88	.9	4.17	4.82	9.62	8.99	4.15	33.03	0.369
4 D 0.1WB	4.44	1.04	1.6	4.44	4.57	9.56	9.01	4.31	33.12	3.69
5 D 0.2WB	4.90	.09	1.4	5.72	5.18	9.10	10.90	3.80	33.02	7.38
6 D 0.2VA	4.45	1.91	.7	4.18	4.93	9.55	9.11	4.24	32.82	.211
7 D 0.1VA	4.41	1.95	.8	4.16	4.88	9.59	9.04	4.19	32.93	1.06
8 D 0.5VA	4.38	.94	5.3	4.47	4.05	9.62	8.52	4.62	33.33	5.28
9 D 0.1K	4.40	1.80	1.2	4.19	4.70	9.60	8.89	4.31	32.99	.276
10 D 0.5K	4.40	1.76	3.4	4.21	4.25	9.60	8.46	4.74	33.01	1.38
11 D 2.0K	4.30	1.44	13.6	4.27	3.65	9.70	7.92	4.98	33.37	5.52
12 D 1.0MS	4.47	1.67	.6	4.25	5.00	9.53	9.25	4.16	32.84	.264
13 F NASA	4.29	1.21	.0	4.35	----	9.71	----	----	33.48	----
14 F NASB	4.40	1.20	.0	4.37	----	9.60	----	----	33.47	----
15 F 0.01WB	4.38	1.14	.0	4.39	----	9.62	----	----	33.25	.369
16 F 0.1WB	4.72	.20	.5	5.26	5.08	9.28	10.34	3.82	33.10	3.69
17 F 0.2WB	5.35	.24	2.5	5.81	4.38	8.65	10.19	5.86	31.76	7.38
18 F 0.02VA	4.30	1.25	.4	4.34	5.18	9.70	9.52	3.38	33.44	.211
19 F 0.1VA	4.31	1.06	1.4	4.41	4.63	9.69	9.04	3.89	33.48	1.06
20 F 0.5VA	4.85	.19	1.0	5.36	4.78	9.15	10.14	4.41	32.81	5.28
21 F 0.1K	4.38	1.26	1.4	4.35	4.63	9.62	8.98	4.16	33.21	.276
22 F 0.5K	4.54	1.13	3.7	4.44	4.21	9.46	8.65	4.97	32.82	1.38
23 F 2.0K	4.48	.80	13.4	4.57	3.65	9.52	8.22	5.22	33.13	5.52
24 F 1.0MS	4.35	1.19	.3	4.37	5.30	9.65	9.67	3.38	33.32	.264
25 G NASA	4.46	.70	.0	4.62	----	9.54	----	----	33.24	----
26 G NASB	4.43	.98	.0	4.47	----	9.57	----	----	33.18	----
27 G 0.01WB	4.53	.57	.0	4.73	----	9.47	----	----	33.14	0.369
28 G 0.1WB	5.97	.09	.9	7.43	4.82	8.03	12.25	5.66	31.52	3.69
29 G 0.2WB	6.65	.18	.9	9.28	4.82	7.35	14.10	5.85	31.33	7.38
30 G 0.02VA	4.42	.61	.6	4.67	5.00	9.58	9.67	3.59	33.41	.211
31 G 0.1VA	4.55	.55	1.2	4.75	4.70	9.45	9.45	4.20	33.10	1.06
32 G 0.5VA	5.64	.00	3.9	----	4.19	8.36	----	----	----	5.28
33 G 0.1K	4.48	.66	1.4	4.65	4.63	9.52	9.28	3.92	33.21	.276
34 G 0.5K	4.67	.52	2.4	4.82	4.40	9.33	9.22	4.79	32.81	1.38
35 G 2.0K	4.70	.27	7.7	5.12	3.89	9.30	9.01	5.09	33.02	5.52
36 G 1.0MS	4.46	.43	.0	4.83	----	9.54	----	----	33.45	.264
37 H NASA	4.46	.48	.0	4.79	----	9.54	----	----	33.41	----
38 H NASB	4.55	.42	.0	4.87	----	9.45	----	----	33.22	----
39 H 0.01WB	4.64	.34	.4	4.99	5.18	9.36	10.17	3.75	33.07	.369
40 H 0.1WB	6.40	.11	.7	8.59	4.93	7.60	13.52	5.68	31.39	3.69
41 H 0.2WB	6.90	.23	1.2	10.14	4.70	7.10	14.84	5.86	31.44	7.38
42 H 0.02VA	4.52	.46	.4	4.82	5.18	9.48	10.00	3.56	33.26	.211
43 H 0.1VA	4.66	.27	1.2	5.10	4.70	9.34	9.80	4.18	33.12	1.06
44 H 0.5VA	5.95	.09	4.2	7.38	4.16	8.05	11.54	6.31	31.53	5.28
45 H 0.1K	4.64	.31	1.7	5.03	4.55	9.36	9.58	4.34	33.11	.276
46 H 0.5K	4.87	.30	3.3	5.17	4.26	9.13	9.43	5.18	32.56	1.38
47 H 2.0K	5.15	.05	9.7	6.22	3.79	8.85	10.01	5.44	32.77	5.52
48 H 1.0MS	4.61	.40	.3	4.91	5.30	9.39	10.21	3.62	33.08	.264

isoelectric point of 4.3, should have had little effect on the pH's of the solutions containing it.

As shown in the section on Al_b measurements, those solutions that are here shown to be supersaturated with respect to aluminum silicate showed very rapid decreases in Al_b concentrations. Within 2–5 days Al_b was below the approximately 10^{-6} molar detection limit, with only two or three points to trace the rate of polymerization. As to whether this sudden decrease is really due to surface catalyzed polymerization to form gibbsite or to reaction of the aluminum hydroxide polymer

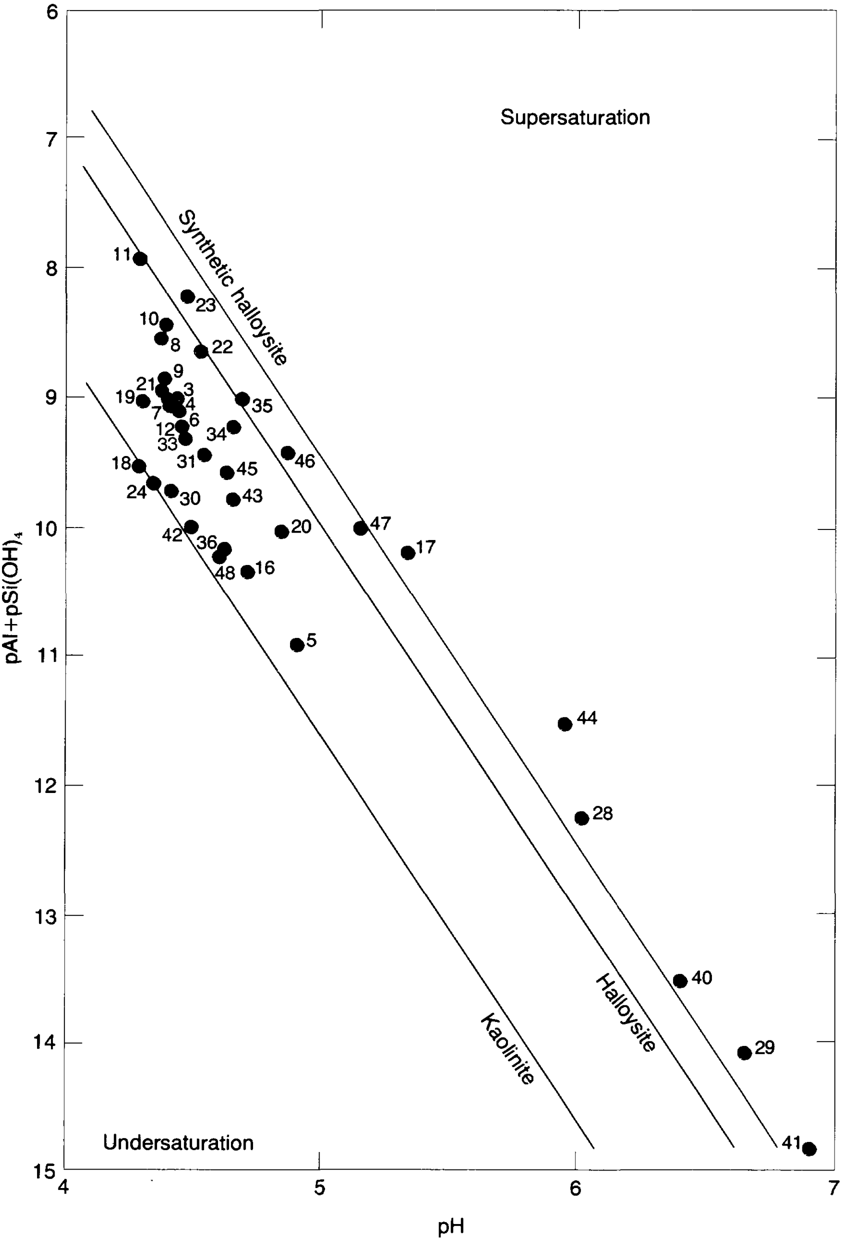

FIGURE 5.—Clay-mineral solubilities compared with compositions of experimental solutions. Numbers beside points correspond to solutions likewise numbered in table 5.

with silica released from the surfaces, we can say with some certainty that in the cases mentioned, the clay mineral surfaces have caused chemical interferences and have introduced factors other than those of an inert surface catalyzing aluminum hydroxide polymerization. Because of this effect, those solutions calculated to be supersaturated or near saturation with respect to aluminosilicates will not be further studied for comparison of polymerization rates and rate constants. However, since the effects of aluminosilicate solubility most likely become dominant only after several weeks aging and any adsorption of Al_a or Al_b by the surface took place after only a few hours, as later shown, the adsorption of Al_a and Al_b in these solutions can be considered.

GIBBSITE EQUILIBRIUM SOLUBILITY

The solubility constant for gibbsite given by Smith and Hem (1972) for the expression $K=[Al^{+3}]\,[H^{+}]^{-3}$ is $10^{8.22}$. This represents the behavior of well-crystallized material produced by long aging (more than 2 years in some instances). If written as a conventional solubility product,

$$K_{s0}=[Al^{+3}][OH^{-}]^{3},$$

this becomes $10^{-33.78}$. Hem and Roberson (1967) reported a value for this solubility product of $10^{-32.65}$, representing microcrystalline gibbsite. Their solid was aged for a shorter time.

Values are given in table 5 for K_{s0} for solutions D, F, G, and H after 2–3 months of aging. The activity products for these systems lie between the K_{s0} values for microcrystalline gibbsite and the more stable final form. This is illustrated in another way by plotting $-\log[Al^{+3}]$ versus pH in figure 6.

A few points would have plotted substantially to the right (supersaturation) of even the microcrystalline gibbsite line. These are for solutions that gave evidence of attack on the surfaces and cannot be considered significant when treated in this simplified equilibrium model.

In general the positions of the points where effects of silica are absent are about what would be predicted for the length of aging, using the criteria of Smith and Hem (1972). As the solutions age, it would be expected the points would move toward the left hand gibbsite solubility limit.

Although the data in tables 1–5 show a considerable loss in Al_a occurred when the surfaces were present, the behavior of Al_a generally seems to fit that of a gibbsite equilibrium system. A more detailed examination of the data is obviously required before the behavior of Al_a can be fully explained.

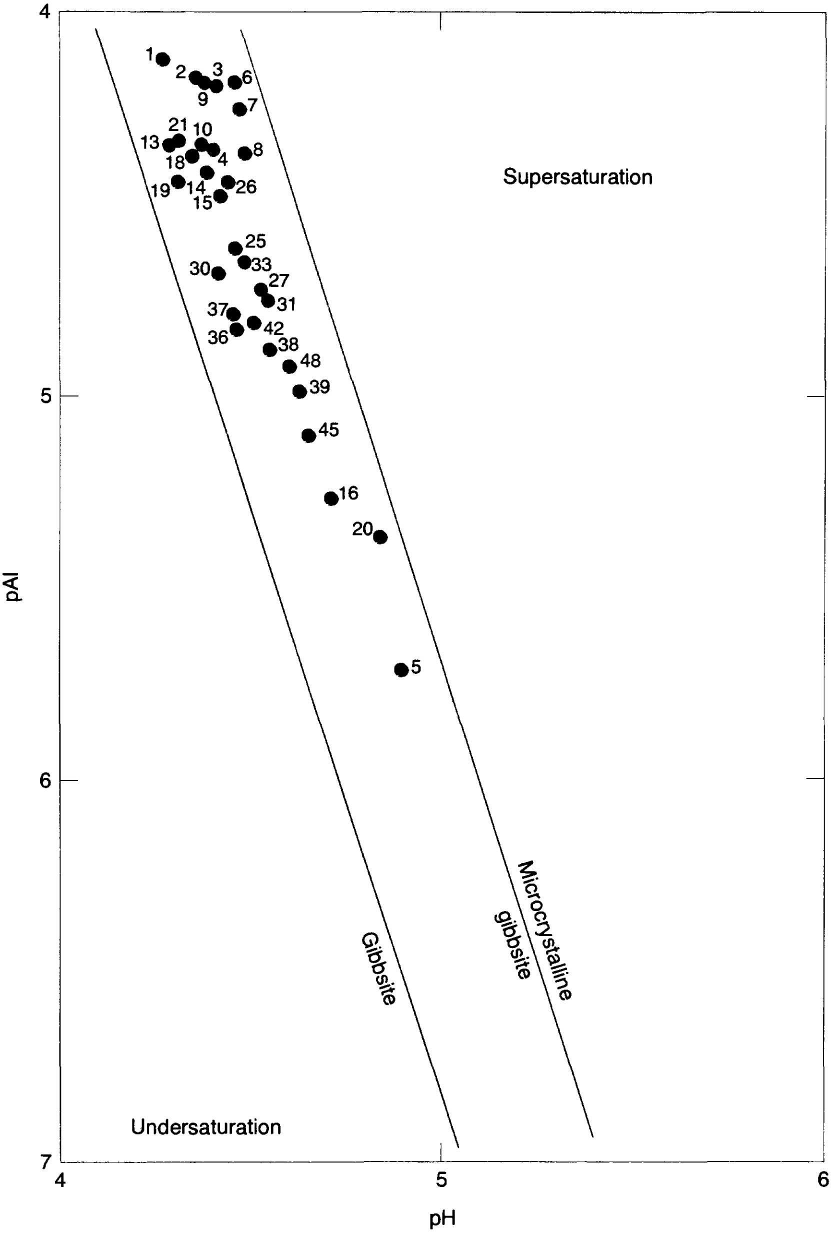

FIGURE 6.—Gibbsite solubilities compared with compositions of experimental solutions. Numbers beside points correspond to solutions likewise numbered in table 5.

CHANGES IN pH DURING AGING

Smith and Hem (1972) observed a substantial decrease in pH during aging of their solutions when the ratio of bound hydroxide to aluminum was 0.94 or greater. This decrease was attributed to the process of polymerization of Al_b, and they were able to demonstrate a stoichiometric relationship. In solutions where polymerization did not occur, the pH remained essentially constant. The approach of the solutions to equilibrium with respect to gibbsite occurred mainly through the decreasing pH. It is of interest to compare pH changes in the solutions having mineral surfaces with corresponding ones that had no mineral surfaces.

Although the solutions D, F, G, and H prepared for this work were made by mixing amounts of stock solutions that were identical to those used by Smith and Hem (1972), the composition of the final mixtures differed somewhat from those of the earlier study. The stock solutions were mixed slowly with the aim of maximizing the Al_b concentration. As a result the Al_b content was substantially higher, Al_a somewhat lower, and pH a little lower than in corresponding solutions of the earlier study. As noted by Smith and Hem (1972), slow addition of the basic solution during mixing tends to produce a solution farther from equilibrium than rapid addition does, in that slow addition promotes the formation of Al_b, a nonequilibrium species.

The solutions that did not contain added mineral surfaces did generally follow the previously observed patterns after mixing. The pH usually decreased in these solutions by an amount similar to that observed by Smith and Hem in the first 100 days that their solutions were aged.

The values of pH observed in the final analysis of our aging solutions, made after about 100 days of aging, are given in table 5. It is evident that the solutions to which the larger amounts of solid minerals were added generally had a higher pH after aging than the other solutions. Furthermore, the observations of pH made during aging (tables 1–4) show that many of these solutions had only small changes in pH after the initial observation, made just after time zero when the solutions were first prepared and mineral surfaces were added.

It seems obvious that the mineral surfaces influenced the aging process in some way; however, the systems involved are more complex than those discussed in Smith and Hem (1972), and several possible processes may have been involved. As previously stated, actual attack and partial dissolution of the surfaces probably occurred in some of the solutions, resulting in losses of H^+ by reaction with surficial material.

Also, reactions involving aluminosilicate precipitation could occur. The final equilibrium condition might thus be shifted away from one involving only gibbsite. Another possible effect is the adsorption of cations by the mineral surface. Direct sorption of H^+ would, of course, increase the pH, and preferential sorption of any of the various forms of aqueous aluminum also would have indirect effects on pH. It is noteworthy that the solutions with highest pH generally are the ones in each group with large exchange capacity associated with bentonite and volcanic ash; the solutions containing the largest amount of kaolinite show a less prominent pH increase. In any event, these are only three of possibly several causes for differences observed in these solutions.

The effects of adsorption and cation exchange on aluminum species concentrations will be considered later in this paper.

CHANGES IN Al_a AND Al_b CONCENTRATION DURING AGING

As mentioned earlier, measurements of aqueous Al_a and Al_b were made periodically on each group of solutions. In the analytical procedure where no surfaces have been added to the solution, the amount of Al_c is calculated by difference, since it is assumed that $\Sigma Al = Al_a + Al_b + Al_c$.

It should be noted that the Al_a species concentration is a directly determined value. Differences between the Al_a content of the blank solution and the solutions containing surfaces, therefore, are valid measurements of the Al_a losses (or ΔAl_a). The results may be used to evaluate the nature and rates of processes at the mineral surfaces that are responsible for the loss of aqueous Al_a.

Similarly, aqueous Al_b can be measured in a somewhat less direct way, and ΔAl_b can be computed by comparing values for the blank solution with the comparable values for solutions containing surfaces. If there are significant differences in behavior of Al_a and Al_b, the experimental results should permit at least a generalized evaluation.

The third form of aqueous aluminum evaluated by Smith and Hem (1972), Al_c, presents more difficult problems. In the absence of surfaces, it can perhaps be assumed, as was done previously, that the difference between the total initial aluminum concentration and the measured values of $Al_a + Al_b$ at time *t* represents the concentration of Al_c. This material is in the colloidal size range, or near it, and cannot be directly measured, even where solid mineral surfaces are not present, although qualitative evidence of its presence is readily obtainable. When surfaces are present, there is still another species of aluminum to be considered, the adsorbed aluminum, which cannot be readily determined separately from the Al_c. The total of both can be calculated as the difference between $Al_a + Al_b$ and the total initial aluminum for any of the solutions at a specific time after the surface was added.

Changes in the concentration of Al_a between 1 and 100 days were observed in many of these solutions, although the changes generally were small. Smith and Hem (1972) reported no change of significance occurred in Al_a in their solutions during aging.

It does not seem possible to attribute much significance to the changes in Al_a that can be seen in tables 1–4. Some solutions show small gains in Al_a, and others show losses. There is no clear-cut relationship to amount or kind of solid present. Some depolymerization of aqueous Al_b or desorption of aluminum species might have occurred as the pH changed during aging and polymerization.

The Al_b contents show a much more consistent trend and, as in the solutions containing no added surface, the trend was downward throughout the aging period.

Smith and Hem (1972) observed a first-order disappearance of Al_b over a considerable part of the aging period, and the half-time of this process appears from their data to have been about 20 days. However, the Al_b content of most of their solutions changed much more slowly during the first 20 days than during the next 100 days, where the first-order rate mechanism was well defined.

Values of log Al_b concentration and time in days were taken from tables 1–4 and plotted. The results for solutions in the F, G, and H series generally correspond to those obtained by Smith and Hem, in that the data generally show a first-order rate mechanism and the half-time of the process is about 20 days. Most of the solutions in the D series lost very little Al_b during 103 days of aging. The initial pH of these D solutions was in a range where Smith and Hem's result shows little polymerization took place during an equivalent period of time.

Typical graphs of log Al_b concentration versus time in days are given as figures 7 and 8. The polymerization rate is evidently not significantly influenced by the presence of mineral surfaces of the types used here. However, the surfaces do have a readily discernible effect in the early part of the aging process, because the amount of Al_b present at the time of the first measurement can be seen in tables 1–4 to differ from one solution to another and the lower values represent solutions to which mineral surfaces had been added. A closer study of the effects produced immediately upon addition of the solid materials seems, therefore, to be required.

CONCENTRATION OF Al_b AT TIME ZERO

From examining first-order rate curves drawn across the plots of $-\log(Al_b)$ versus age time, it can be observed that the value for $-\log(Al_b)$ at zero age time, that is immediately after addition of mineral

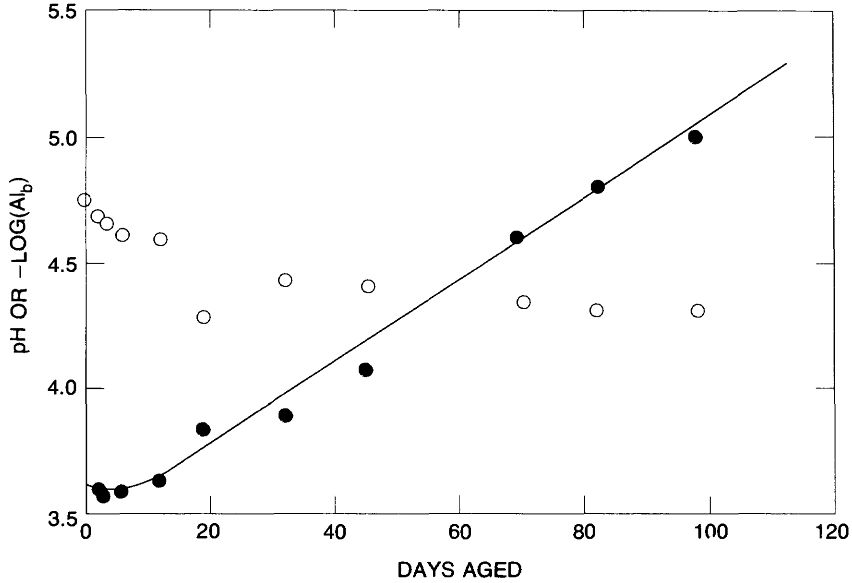

FIGURE 7.—First-order disappearance of Al_b, pH (circles) and $-\log(Al_b)$ (dots) as a function of aging time for representative solution F 0.02VA.

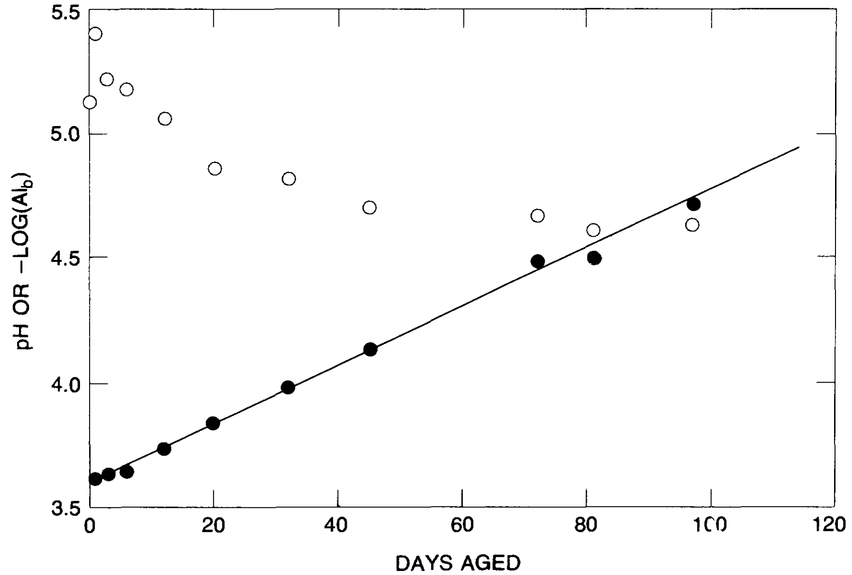

FIGURE 8.—First-order disappearance of Al_b, pH (circles) and $-\log(Al_b)$ (dots) as a function of aging time for representative solution H 0.1K.

surfaces, varies widely within a given set of solutions. This initial value appears to be dependent on the amount and type of surface added.

Within each set of solutions, those with no added surface contained greater Al_b concentrations than any of the ones to which mineral surfaces were added. This indicates that on addition of surface, a substantial amount of Al_b was lost. Because the first-order polymerization rates are too slow to account for such rapid polymerization during the 1 or 2 days before the first analysis, this loss of Al_b is probably attributable to adsorption by the surface. If the difference in initial values of $-\log(Al_b)$ is attributable to adsorption by the surface, the amount adsorbed, in terms of concentration, may be calculated by subtracting the Al_b concentration in question from the Al_b concentration of the solution to which no surface was added. This quantity is shown in the last column of table 6.

From data in table 6, it appears that the greatest losses of Al_b occurred in solutions containing the greatest area of solid surface. The relationship between Al_b loss and surface area is demonstrated in figures 9–12. Although some of the points deviate from the regression lines, the results suggest that differences in the properties of the mineral surfaces used in this study are of relatively small significance and loss of Al_b is primarily related to area of surface available.

Smith and Hem (1972, p. 32) attributed the decline in pH that they observed in their solutions during aging to the production of Al_c by polymerization of Al_b. A somewhat similar decline can be seen in the pH of solutions without the added surface listed in tables 1–4 of this paper. However, the solutions to which mineral surfaces were added do not show pH changes that correlate with Al_b loss. From data in tables 1–4, it is evident that most solutions where Al_b loss occurred immediately after the surfaces were added did not decrease in pH to the extent one might expect had the Al_b polymerization gone to completion at the surface. It would seem, therefore, that the loss of Al_b represents an adsorption rather than catalysis of the polymerization process.

It is possible the surfaces also adsorbed some H^+ and thus influenced the pH. This effect cannot be completely evaluated, but it is believed to be minor. The solutions with surfaces in which Al_b loss continued during aging decreased in pH, suggesting that the effect of the polymerization reaction can be observed, when it occurs, even if the surfaces are present.

SIGNIFICANCE OF CATION EXCHANGE CAPACITY

The CEC (cation exchange capacity) of added surfaces is shown in

TABLE 6.—*Short-term losses of* Al_b *in solutions D, F, G, and H*

[Dash leaders indicate Al_b loss so rapid that Al_b at time zero could not be confidently extrapolated]

Solution	Added surface area (m^2/l)	Extrapolated $-\log Al_b$		Concentration differences (moles/litre $\times 10^4$)
D NASA	0.0	3.70	mean,	0.00
D NASB	.0	3.67	3.68	
D 0.01WB	22	3.94		.94
D 0.1WB	220	4.90		1.96
D 0.2WB	440	----		----
D 0.02VA	8.8	3.72		.18
D 0.1VA	44	4.07		1.24
D 0.5VA	220	----		----
D 0.1K	6.0	3.76		.35
D 0.5K	30	3.89		.80
D 2.0K	120	4.49		1.77
D 1.0MS	2.0	3.66		.00
F NASA	.0	3.50	mean,	.00
F NASB	.0	3.50	3.50	
F 0.01WB	22	3.75		1.38
F 0.1WB	220	----		----
F 0.2WB	440	----		----
F 0.02VA	8.8	3.65		.92
F 0.1VA	44	3.78		1.50
F 0.5VA	220	----		----
F 0.1K	6.0	3.65		.92
F 0.5K	30	3.83		1.68
F 2.0K	120	4.60		2.91
F 1.0MS	2.0	3.57		.47
G NASA	.0	3.53	mean,	.00
G NASB	.0	3.55	3.54	
G 0.01WB	22	3.67		.75
G 0.1WB	220	6.08		2.88
G 0.2WB	440	----		----
G 0.02VA	8.8	3.58		.25
G 0.1VA	44	3.72		.98
G 0.5VA	220	3.72		.98
G 0.1K	6.0	3.58		.25
G 0.5K	30	3.70		.89
G 2.0K	120	4.3		2.38
G 1.0MS	2.0	3.56		.13
H NASA	.0	3.58	mean,	.00
H NASB	.0	3.58	3.58	
H 0.01WB	22	3.69		.59
H 0.1WB	220	4.65		2.41
H 0.2WB	440	----		----
H 0.02VA	8.8	3.65		.39
H 0.1VA	44	3.78		.97
H 0.5VA	220	4.63		2.40
H 0.1K	6.0	3.63		.29
H 0.5K	30	3.85		1.22
H 2.0K	120	5.0		2.53
H 1.0MS	2.0	3.60		.12

table 5 for each solution. The exchange positions on the surfaces present would, of course, be occupied at all times by cations taken up from the associated solution. Moreover, the nature of the ions so held and the proportions of species in the exchange positions would be functions of the solution composition as well as of properties of the exchange sites.

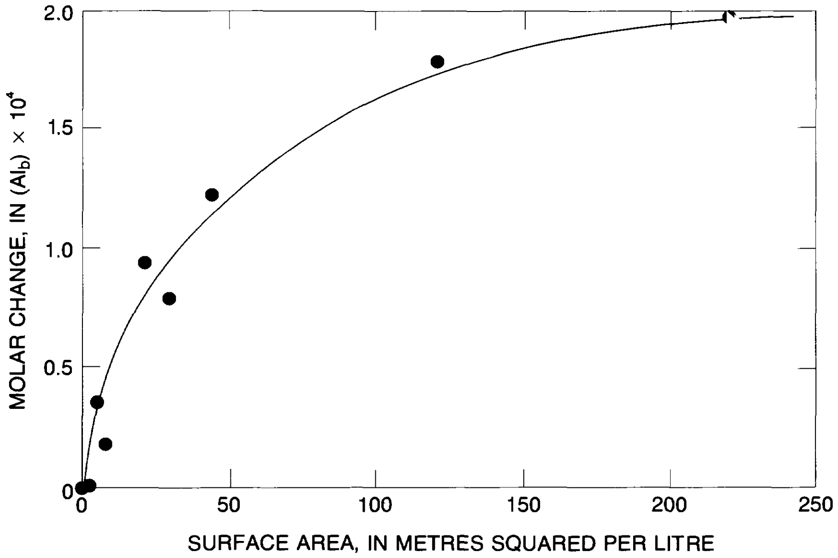

FIGURE 9.—Initial loss of Al_b due to apparent short-term adsorption from solutions D as a function of effective area of surface added.

Cation exchange reactions are generally rapid and can be treated quantitatively by equilibrium chemical models. A completely quantitative treatment, however, becomes difficult in a system containing several different cationic species. In the absence of aluminum, the cation exchange positions would be occupied by sodium and hydrogen ions in the proportion dictated by pH and the specific behavior of the exchange sites. In a sense, the PZC (point of zero charge) measurement characterizes the behavior of a surface toward H^+; surfaces with high PZC, such as bentonite and volcanic ash, should retain H^+ more strongly in the neutral or mildly acid pH range than would be expected for the kaolinite surface which has a much lower PZC.

The CEC values for the aging-study solutions range from 0.211×10^{-4} to 7.38×10^{-4} equivalents per litre. The CEC is considered negligible for the solutions to which no solid was added. By comparing CEC values with the concentrations of aluminum available in the test solutions, some indication of the potential importance of ion exchange processes can be gained. In the solutions containing 0.50 g of volcanic ash, the CEC is sufficient to take up almost all the aluminum as Al^{+3}, and substantial fractions of total aluminum could be adsorbed in several other solutions. Also, the capacity for H^+ adsorption is significant.

SHORT-TERM ADSORPTION EXPERIMENTS

To study more closely the rate and magnitude of the apparent initial

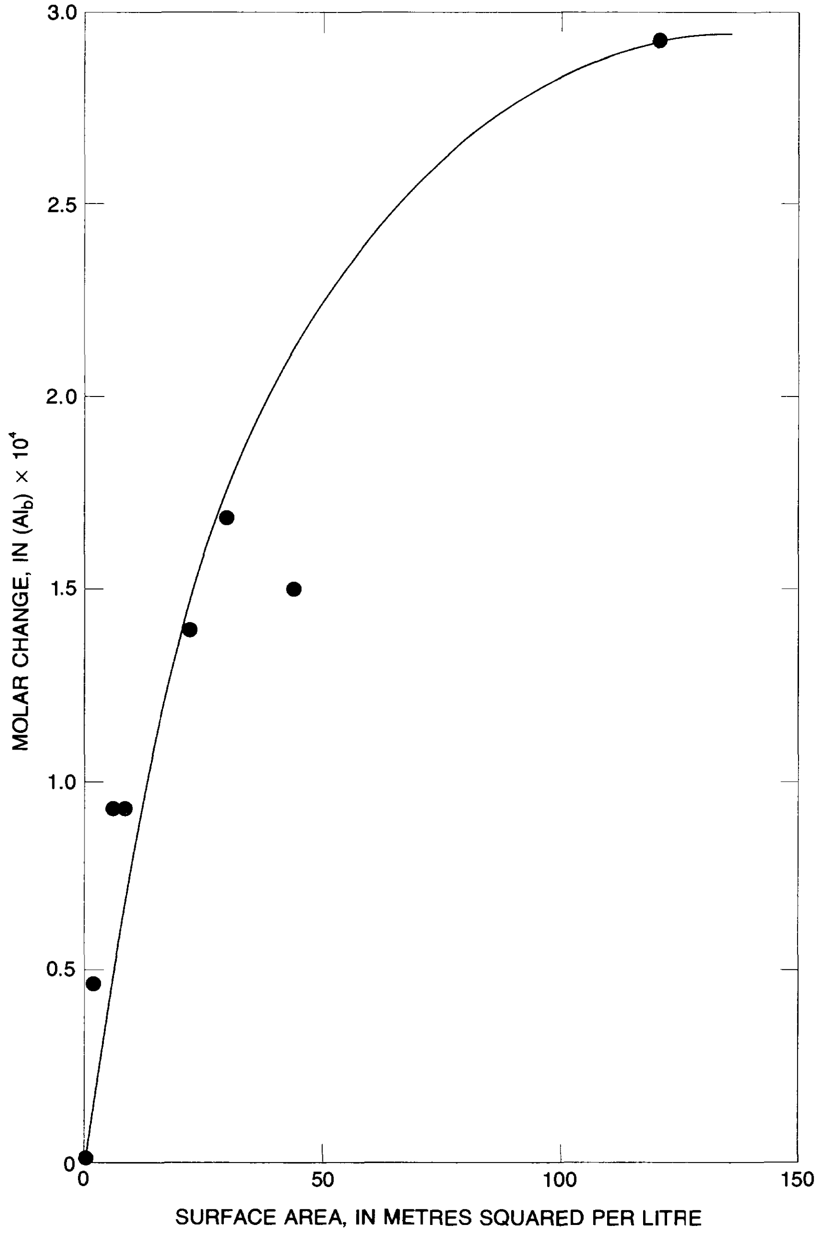

FIGURE 10.—Initial loss of Al_b due to apparent short-term adsorption from solutions F as a function of effective area of surface added.

adsorption of Al_a and Al_b, 3,000 ml of solution DS (r_n=1.40) were made and divided into 12 250-ml aliquots. A solution having this low an r_n

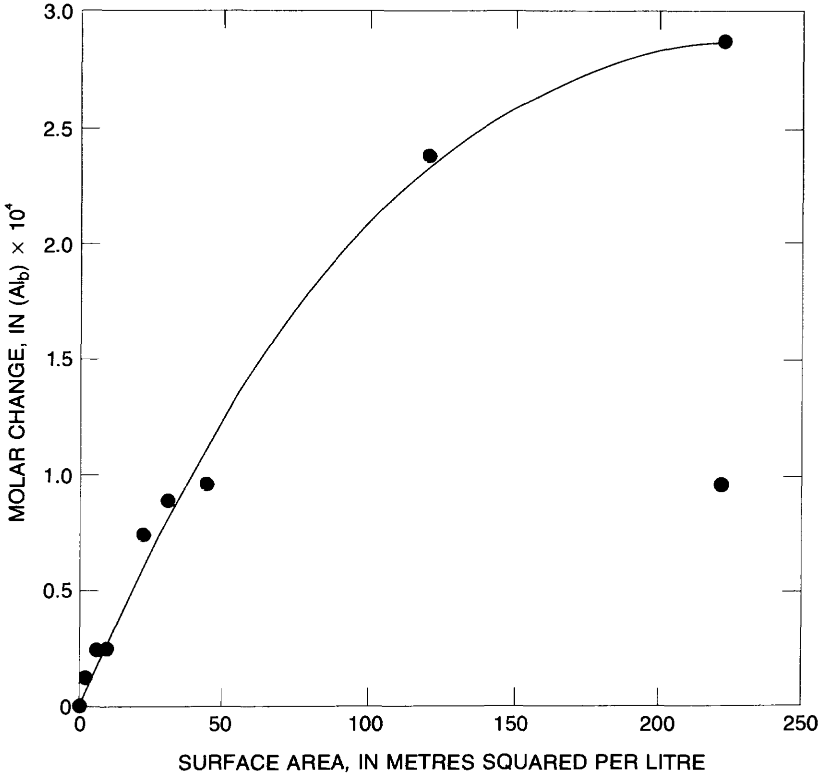

FIGURE 11.—Initial loss of Al_b due to apparent short-term adsorption from solutions G as a function of effective area of surface added.

value was used here because the rate of Al_b polymerization is slow under these conditions. Therefore, any sudden disappearance of Al_b would most likely be attributable to adsorption by the surface. The amounts of solids added were 0.010, 0.030, 0.10, and 0.20 gram Wyoming bentonite, 0.020, 0.050, 0.10, and 0.50 g volcanic ash, and 0.10, 0.50, and 2.0 g kaolinite. One solution was left untreated to act as a blank. These 12 solutions were then placed on a wrist-action shaker and shaken vigorously for 48 hours. Aliquots were withdrawn and analyzed for Al_a and Al_b at 1, 4, 32, and 48 hours age time and also were analyzed for total aqueous aluminum at 48 hours. These aliquots were centrifuged for 5 minutes at 2,000 *G*'s prior to analysis in order to separate the suspended clays. (Comparison of Al_a, Al_b, and Al_c analyses for a centrifuged and a noncentrifuged aliquot of the blank showed that no important quantity of aqueous aluminum was lost by this centrifuging.) They were then analyzed for Al_a and Al_b using the analytical procedure previously described, and aqueous Al_c was calculated by difference from the total aqueous aluminum determined after

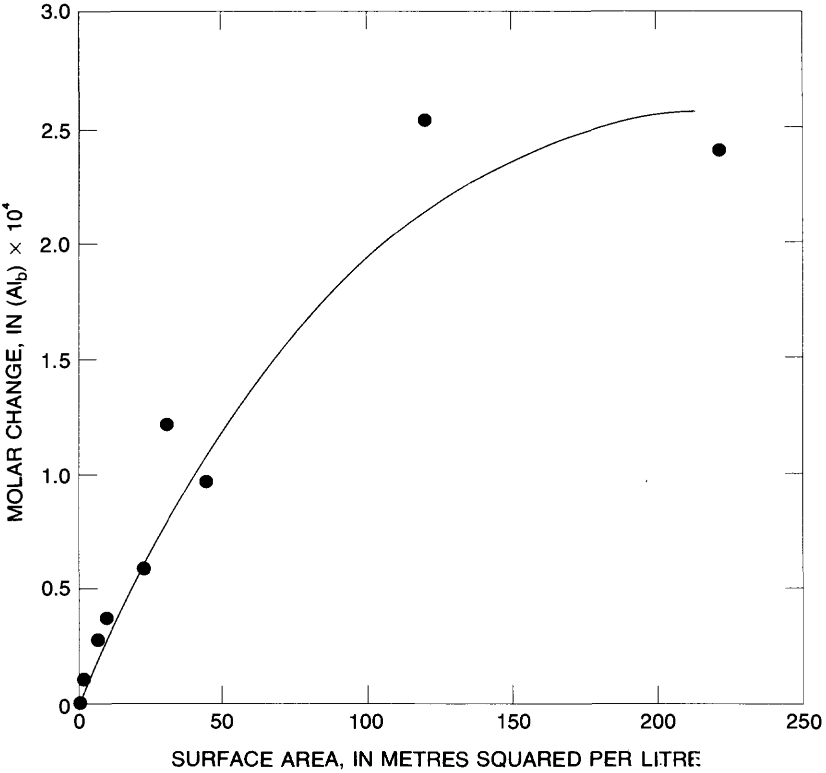

FIGURE 12.—Initial loss of Al_b due to apparent short-term adsorption from solutions H as a function of effective area of surface added.

48 hours. Also at 48 hours silica content and pH were measured in order to determine the extent of dissolution of solids and possible interference at that time and also to be able to determine the distribution of the four Al_a monomeric species. The pH values ranged from 4.32 for DS 2.0K to 4.67 for DS 0.2WB. The blank solution had a pH of 4.45. Silica concentrations at 48 hours were low, the highest being 0.18 mg/l SiO_2 for DS 2.0K.

From these data it was concluded the dissolution of the added minerals was negligible and aluminosilicate reactions did not need to be considered. For each solution the amounts of Al_a, Al_b, and Al_c adsorbed were calculated by subtracting their concentrations from those for the blank (DS NAS), defined to have zero surface area and no aluminum loss by adsorption. Although we know that loss of Al_b within a 48-hour span is unlikely to be caused by increased polymerization of Al_b to form more Al_c as Al_c is adsorbed, we may not be able to assume the same for Al_a with respect to Al_b. Since we have not thoroughly examined the kinetics of formation of Al_b from Al_a, we have no direct experimental evidence to show whether loss of Al_a is due to adsorption or to polymerization to form more Al_b to compensate for the Al_b adsorbed. If the latter were the case, actual adsorption of Al_a would have been somewhat less and Al_b adsorption somewhat more than expressed here. The methods used here to calculate adsorbed Al_a and Al_b may be slightly suspect in that they are based on an adsorption assumption where there is no such interaction between Al_a and Al_b species. The experimental and calculated aluminum values are given in tables 7 and 8.

ADSORPTION OF Al_a

Al_a, unlike species Al_b and Al_c, can be completely defined in terms of species concentrations and effective ionic charge if the pH is known. The concentrations of $Al(H_2O)_6{}^{+3}$, $AlOH(H_2O)_5{}^{+2}$, and $Al(OH)_2(H_2O)_4{}^{+}$ are calculated from Al_a concentration and pH using the equilibrium relationships and activity coefficients quoted earlier in this paper; $Al(OH)_4(H_2O)_2{}^{-}$ is negligible below pH 5.0. The calculated values are given in table 9. At 48 hours the pH values observed in the solutions ranged from 4.35 to 4.67, and most of the Al_a in all the solutions was in the form $Al(H_2O)_6{}^{+3}$ at this low pH.

From the data on Al_a and pH at 48 hours, it is possible to gain some further insight into the nature of the process by which this form of aluminum is taken up by the mineral surfaces. In a general way it is obvious that solutions with the larger amounts of mineral surface area show the larger losses of Al_a. The relationship between surface area and loss of Al_a is rather well defined, as shown by the plots in figure 13, in which the points lie close to a straight line at 48 hours and have almost the same relationship at 1 hour.

The ion exchange sorption mechanism can be explored by a mass law equilibrium model. For the systems to be examined, the cationic species present are Na^+, H^+, and the three Al_a monomers, and as noted, the trivalent aluminum ion is predominant. At the pH range of these solutions, the sodium activity is not sufficiently great to retain a significant amount of sodium in exchange sites on the solid surfaces. Consequently, the system can be considered as involving H^+ and Al^{+3} in solution and adsorbed on the surfaces. Whether the Al^{+3} ion itself is reversibly adsorbed at exchange sites or the reaction is more complex, involving the conversion of Al^{+3} to hydroxide complexes, can also be studied, but without directly measuring all the species.

The surfaces in some of the solutions have a CEC sufficient to adsorb much more H^+ than the active free concentration represented by the pH, and as noted earlier, the pH in some of the solutions probably shows this influence. The kaolinite surfaces may have carried enough sorbed H^+ when they were introduced to explain the lower pH's ob-

TABLE 7.—*Adsorption experiment data*

A. Molar Al_a *concentration* $\times 10^4$

Solution	1 hour	4 hours	32 hours	48 hours
DS NAS	2.14	2.22	2.11	2.08
DS 0.01WB	2.08	2.18	2.00	2.06
DS 0.03WB	1.77	2.07	1.96	1.74
DS 0.1WB	1.34	1.30	1.28	1.30
DS 0.2WB	.39	.26	.31	.45
DS 0.02VA	2.06	2.16	2.03	2.06
DS 0.05VA	2.01	2.15	1.97	2.05
DS 0.1VA	1.83	1.85	1.87	1.91
DS 0.5VA	1.02	1.10	1.12	1.12
DS 0.1K	1.95	2.11	1.97	1.96
DS 0.5K	1.91	2.02	1.91	1.92
DS 2.0K	1.70	1.81	1.86	1.86

B. Molar Al_b *concentration* $\times 10^4$

Solution	1 hour	4 hours	32 hours	48 hours
DS NAS	1.87	1.84	1.90	1.94
DS 0.01WB	1.51	1.45	1.54	1.54
DS 0.03WB	.96	.69	.75	.70
DS 0.1WB	.11	.14	.17	.14
DS 0.2WB	.06	.03	.02	.01
DS 0.02VA	1.63	1.61	1.65	1.63
DS 0.05VA	1.53	1.38	1.38	1.38
DS 0.1VA	1.22	.99	.98	.92
DS 0.5VA	.18	.15	.13	.13
DS 0.1K	1.79	1.60	1.77	1.77
DS 0.5K	1.51	1.40	1.42	1.27
DS 2.0K	.42	.34	.36	.29

C. Other analyses at 48 hours

Solution	Total aqueous Al, molar $\times 10^4$	pH	SiO_2 (mg/l)
DS NAS	4.71	4.46	0.00
DS 0.01WB	4.20	4.45	.03
DS 0.03WB	2.82	4.47	.01
DS 0.1WB	1.51	4.46	.05
DS 0.2WB	.35	4.67	.03
DS 0.02VA	4.30	4.48	.02
DS 0.05VA	3.78	4.45	.02
DS 0.1VA	3.17	4.44	.04
DS 0.5VA	1.37	4.41	.07
DS 0.1K	4.34	4.48	.02
DS 0.5K	3.80	4.40	.06
DS 2.0K	2.25	4.35	.18

TABLE 8.—*Calculated sorbed species and aqueous* Al_c *concentrations*

[Concentrations expressed in moles/litre $\times 10^4$; sorbed species are expressed in terms of the concentration change effected by the addition of the surface. For solution DS NAS, sorbed concentration is defined as zero for all species]

Solution	Sorbed			Added surface area (m^2/l)	Cation exchange capacity (equivalents/l $\times 10^4$)	Aqueous Al_c
	Al_a	Al_b	Al_c			
				1 hour		
DS NAS	0.00	0.00	----	0.0	0.0	----
DS 0.01WB	.06	.36	----	22	.37	----
DS 0.03WB	.37	.91	----	66	1.11	----
DS 0.1WB	.80	1.76	----	220	3.69	----
DS 0.2WB	1.75	1.81	----	440	7.38	----
DS 0.02VA	.08	.24	----	8.8	.21	----
DS 0.05VA	.13	.34	----	22	.53	----
DS 0.1VA	.31	.65	----	44	1.06	----
DS 0.5VA	1.12	1.69	----	220	5.28	----

Solution	Sorbed			Added surface area (m^2/l)	Cation exchange capacity (equivalents/l × 10^4)	Aqueous Al$_c$
	Al$_a$	Al$_b$	Al$_c$			
			1 hour—Continued			
DS 0.1K	.19	.08	----	6.0	0.28	----
DS 0.5K	.23	.36	----	30	1.38	----
DS 2.0K	.44	1.45	----	120	5.52	----
			4 hours			
DS NAS	0.00	0.00	----	----	----	----
DS 0.01WB	.04	.39	----	----	----	----
DS 0.03WB	.15	1.15	----	----	----	----
DS 0.1WB	.92	1.70	----	----	----	----
DS 0.2WB	1.96	1.81	----	----	----	----
DS 0.02VA	.06	.23	----	----	----	----
DS 0.05VA	.07	.46	----	----	----	----
DS 0.1VA	.37	.85	----	----	----	----
DS 0.5VA	1.12	1.69	----	----	----	----
DS 0.1K	.11	.24	----	----	----	----
DS 0.5K	.20	.44	----	----	----	----
DS 2.0K	.41	1.50	----	----	----	----
			32 hours			
DS NAS	0.00	0.00	----	----	----	----
DS 0.01WB	.11	.36	----	----	----	----
DS 0.03WB	.15	1.15	----	----	----	----
DS 0.1WB	.83	1.73	----	----	----	----
DS 0.2WB	1.80	1.88	----	----	----	----
DS 0.02VA	.08	.25	----	----	----	----
DS 0.05VA	.14	.52	----	----	----	----
DS 0.1VA	.24	.92	----	----	----	----
DS 0.5VA	.99	.77	----	----	----	----
DS 0.1K	.14	.13	----	----	----	----
DS 0.5K	.20	.48	----	----	----	----
DS 2.0K	.25	1.54	----	----	----	----
			48 hours			
DS NAS	0.00	0.00	0.00	----	----	0.69
DS 0.01WB	.02	.40	.09	----	----	.60
DS 0.03WB	.34	1.24	.31	----	----	.38
DS 0.1WB	.78	1.80	.62	----	----	.07
DS 0.2WB	1.63	1.93	.69	----	----	.00
DS 0.02VA	.02	.30	.07	----	----	.61
DS 0.05VA	.03	.56	.34	----	----	.35
DS 0.1VA	.17	1.02	.35	----	----	.34
DS 0.5VA	.96	1.81	.57	----	----	.12
DS 0.1K	.12	.17	.08	----	----	.61
DS 0.5K	.16	.67	.08	----	----	.61
DS 2.0K	.22	1.65	.59	----	----	.10

TABLE 9.—*Calculated aqueous* Al$_a$ *species distribution at 48 hours*

Solution	pH	Molar concentration × 10^4			
		(Al$_a$)	(Al^{+3})	($AlOH^{+2}$)	($Al(OH)_2^{+}$)
DS NAS	4.46	2.08	1.67	0.30	0.11
DS 0.01WB	4.45	2.06	1.65	.30	.11
DS 0.03WB	4.47	1.74	1.38	.26	.10
DS 0.1WB	4.46	1.30	1.04	.19	.07
DS 0.2WB	4.67	.45	.31	.09	.05
DS 0.02VA	4.48	2.06	1.65	.30	.11
DS 0.05VA	4.45	2.05	1.64	.30	.11
DS 0.1VA	4.44	1.91	1.55	.27	.09
DS 0.5VA	4.41	1.12	.92	.15	.05
DS 0.1K	4.48	1.96	1.55	.30	.11
DS 0.5K	4.40	1.92	1.59	.25	.08
DS 2.0K	4.35	1.86	1.58	.22	.06

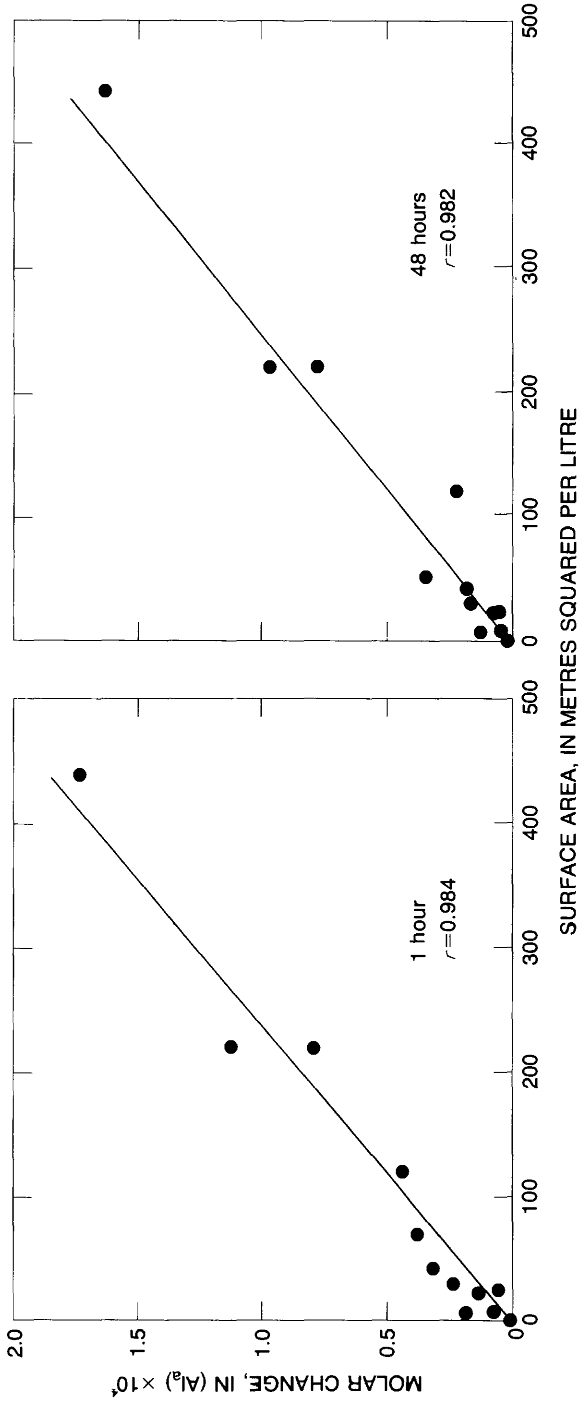

FIGURE 13.—Adsorption of Al_a at 1 hour and 48 hours in solutions DS as a function of effective area of surface added; r is the linear regression correlation coefficient.

served in solutions DS 2.0K and DS 0.5K, and some of the other surfaces may have had other ions in exchange sites that were replaced by H^+ when the solutions were prepared. The higher pH of solution DS 0.2WB might, for example, have been related to exchange of adsorbed Na^+ for H^+. In any event, the equilibrium model, if valid, should be capable of treating H^+-Al^{+3} relationships regardless of the outside influences on pH.

In its simplest form the cation exchange equilibrium might be written

$$Al^{+3}+3H_x \rightleftharpoons 3H^+ + Al_{x3}$$

and

$$\frac{[H^+]^3(Al_{x3})}{[Al^{+3}](H_x)^3}=K_{D3}.$$

The x terms represent adsorbed material, expressed as concentrations in moles per litre. For solutions containing the amounts of the solids shown, the CEC in equivalents per litre is known and can be expressed as

$$CEC=3(Al_{x3})+(H_x).$$

The amounts of adsorbed Al_a shown in the 11 solutions in table 9 were considered to represent Al_x; therefore, the amount of H_x can be calculated for each solution. The value of $[Al^{+3}]$ was computed by multiplying the determined concentration of Al^{+3} by the appropriate activity coefficient for these solutions. If ionic strength is near 0.01, $\gamma_{Al^{+3}}=0.45$. Results of the calculation for K_{D3} (table 10) show a wide range ($10^{-3.62}$ to $10^{+1.45}$) for what is supposed to be a constant. It may be concluded, therefore, that the form of the exchange equilibrium used was not applicable.

The alteration of Al^{+3} to a hydroxide complex at the surface at the time of adsorption could be represented by the equation

$$Al^{+3}+H_2O+2H_x \rightleftharpoons AlOH_{x2}+3H^+$$

or

$$\frac{[H^+]^3(AlOH_{x2})}{[Al^{+3}](H_x)^2}=K_{D2} \text{ on this system,}$$

where

$$CEC=2(AlOH_{x2})+(H_x)$$

and a recalculation of (H_x) is needed. Using this new value for (H_x) and the mass law equation for K_{D2}, a set of K values is obtained with a

TABLE 10.—*Dissolved and sorbed species and selectivity constants for three ion exchange mechanisms (solutions aged 48 hours)*

Solution	$[H^+]$	$[Al^{+3}]$	Al_{ax}	H_x	K_D
DS NAS	$10^{-4.46}$	$10^{-4.13}$	------	------	------
DS 0.01WB	$10^{-4.46}$	$10^{-4.13}$	$10^{-5.70}$	$10^{-4.51}$	$10^{-1.39}$
				$10^{-4.48}$	$10^{-5.96}$
				$10^{-4.46}$	$10^{-10.46}$
DS 0.03WB	$10^{-4.47}$	$10^{-4.21}$	$10^{-4.47}$	$10^{-5.04}$	$10^{+1.45}$
				$10^{-4.37}$	$10^{-4.93}$
				$10^{-4.11}$	$10^{-9.64}$
DS 0.1 WB	$10^{-4.46}$	$10^{-4.33}$	$10^{-4.11}$	$10^{-3.87}$	$10^{-1.55}$
				$10^{-3.67}$	$10^{-5.82}$
				$10^{-3.54}$	$10^{-9.62}$
DS 0.2WB	$10^{-4.67}$	$10^{-4.86}$	$10^{-3.79}$	$10^{-3.60}$	$10^{-2.14}$
				$10^{-3.38}$	$10^{-6.18}$
				$10^{-3.24}$	$10^{-9.70}$
DS 0.02VA	$10^{-4.48}$	$10^{-4.13}$	$10^{-5.70}$	$10^{-4.83}$	$10^{-\ .52}$
				$10^{-4.77}$	$10^{-5.47}$
				$10^{-4.72}$	$10^{-10.29}$
DS 0.05VA	$10^{-4.45}$	$10^{-4.14}$	$10^{-5.52}$	$10^{-4.36}$	$10^{-1.65}$
				$10^{-4.33}$	$10^{-6.07}$
				$10^{-4.30}$	$10^{-10.43}$
DS 0.1VA	$10^{-4.44}$	$10^{-4.16}$	$10^{-4.77}$	$10^{-4.26}$	$10^{-1.15}$
				$10^{-4.14}$	$10^{-5.65}$
				$10^{-4.05}$	$10^{-9.88}$
DS 0.5VA	$10^{-4.41}$	$10^{-4.39}$	$10^{-4.02}$	$10^{-3.62}$	$10^{-2.00}$
				$10^{-3.47}$	$10^{-5.95}$
				$10^{-3.36}$	$10^{-9.50}$
DS 0.1K	$10^{-4.48}$	$10^{-4.16}$	$10^{-4.92}$	<0	------
				$10^{-5.44}$	$10^{-3.32}$
				$10^{-4.85}$	$10^{-9.71}$
DS 0.5K	$10^{-4.40}$	$10^{-4.15}$	$10^{-4.80}$	$10^{-4.05}$	$10^{-1.70}$
				$10^{-3.97}$	$10^{-5.91}$
				$10^{-3.91}$	$10^{-9.94}$
DS 2.0K	$10^{-4.35}$	$10^{-4.16}$	$10^{-4.66}$	$10^{-3.31}$	$10^{-3.62}$
				$10^{-3.29}$	$10^{-6.17}$
				$10^{-3.27}$	$10^{-10.28}$

range of $10^{-6.18}$ to $10^{-3.32}$. This spread is not greatly decreased from the one obtained for K_{D3}.

A further alteration of the equilibrium equation can be made, however, which perhaps is more in accord with what might normally be expected, in that a single Al^{+3} ion is unlikely to neutralize two or three unit surface charges which could be spread some distance apart over the surface. Attachment of the Al^{+3} ion at a single charge site can be represented as

$$Al^{+3}+2H_2O+H_x \rightleftharpoons Al(OH)_{2x}+3H^+,$$

$$\frac{[H^+]^3 Al(OH)_{2x})}{Al^{+3}(H_x)}=K_{D1},$$

and

$$CEC=(Al(OH)_{2x})+(H_x).$$

Recalculation of (H_x) using this model and solving for K_{D1} gave values ranging from $10^{-10.46}$ to $10^{-9.50}$. Although the "constant" still has a fairly wide range, the improvement obtained by postulating a 1:1 exchange of H^+ for Al^{+3} is obvious and suggests that the process takes place in some such fashion. Numerous references in the literature relate the apparent preference for hydroxide complexes over uncomplexed species where polyvalent metals are being adsorbed at inorganic surfaces.

In addition to the cation adsorption process, the activities of Al^{+3} and H^+ also are influenced in these solutions by the precipitation of gibbsite. When the exchange capacity is small compared with the total aluminum present in the system, the adsorbed Al_a species will be withheld at the expense of Al_c, the precipitated form, or Al_b, the metastable potentially precipitable form. Thus at equilibrium both the adsorbed and solid forms could be present. Some of the solutions in this study contained an exchange capacity a little greater than the total molar concentration of aluminum, but the amount of Al_a sorbed at the pH of the solutions was never large enough to preclude gibbsite precipitation. The adsorption of H^+ by the solids tends to obscure the stoichiometry of Al^{+3} and OH^- species involved in complexing or polymerization, and the pH changes in solutions with solid surfaces are not comparable with those where surfaces are absent.

Effects of mineral surfaces on Al_a concentrations can be summarized as follows,

1. Al_a species are adsorbed by the mineral surfaces, and the process appears to follow a cation exchange mass law equilibrium model.
2. The adsorption of Al_a is essentially complete in 1 hour of reaction time.
3. Adsorbed Al_a is produced within the system at the expense of precipitated forms of Al when the solution is initially supersaturated with respect to gibbsite. Gibbsite solubility will control Al_a concentration ultimately unless the exchange capacity is large enough to remove almost all Al_a. Where a large excess of exchange capacity is present, the Al_a concentration may be maintained at a level governed by ion exchange equilibria.
4. Adsorbed Al_a evidently can be desorbed and returned to solution more readily than precipitated Al_c can be redissolved or than polymerized Al_b can be degraded to Al_a.
5. In the process of being adsorbed, Al_a species appear to become essentially monovalent, perhaps through formation of hydroxide complexes at one or more sites in the hydration shell of the Al^{+3} form. In any event, the processes of adsorption and hydrolysis or the first stages of polymerization of Al_a are closely intermingled.

ADSORPTION OF Al_b

Data in table 7 show that in all the 11 solutions that contained mineral surfaces there was significantly less Al_b than in the blank. It is also evident that the loss of Al_b had already mostly taken place before the first set of determinations were made 1 hour after the solutions were prepared and that the changes in aqueous Al_b concentrations are greater on addition of the minerals for the solutions having the greater surface areas. These concentration changes could have resulted from adsorption of Al_b species by the surfaces, or the surfaces might have promoted or catalyzed the polymerization of Al_b to form crystalline gibbsite.

If the latter hypothesis were correct, one would expect a lower pH and a closer approach to the equilibrium solubility of gibbsite in solutions having the larger surface areas and CEC's. In figure 14 the log of the calculated solubility product for $Al(OH)_3$ for each solution is plotted against the log of the CEC in that solution. Although these points are rather scattered, they suggest a trend toward a more stable $Al(OH)_3$ solid is produced by increasing the CEC. For the blank, the value for K_{s0} is $10^{-32.75}$, essentially that of microcrystalline gibbsite.

Although the number of points is rather small, figure 14 does indicate that the three materials have somewhat different effects. Both the kaolinite and volcanic ash surfaces show, as CEC increases, a more

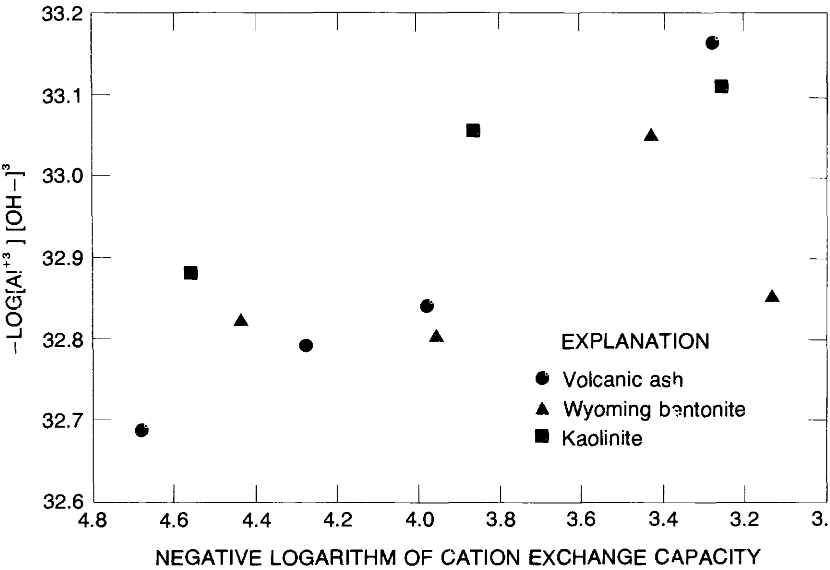

FIGURE 14.—Gibbsite ion activity product in solutions DS as a function of negative logarithm of equivalents of cation exchange capacity added per litre of solution.

strongly decreasing trend in K_{s0} than does the bentonite surface. However, the significance of the apparent correlation is limited and uncertain, because the K_{s0} values for the longer term aging-study solutions do not display a discernible pattern. It can only be concluded that the surfaces may have influenced the early stages of the reactions that precipitated $Al(OH)_3$.

Plots of the changes in concentrations of Al_b as functions of surface area and of CEC (figs. 15, 16) indicate that the adsorption of Al_b is somewhat more closely related to surface area than to CEC. This seems reasonable, because Al_b units are large polymers with a considerable range in net positive charge per included aluminum atom. They cannot be expected to exhibit the same behavior as Al_a species wherein each individual aluminum atom is bound to a charge site. We should, therefore, not expect the adsorbed Al_b to be strictly dependent on the number of surface charge sites, or CEC. The relationship between Al_b adsorption and surface area is linear if Al_b remains in solution in substantial excess. Complete adsorption of Al_b is approached asymptotically if an excess of surface area is present. This behavior is characteristic of adsorption equilibria.

Unlike the adsorption of Al_a, some of the adsorption of Al_b occurs between 1 and 48 hours. The slopes of the linear portions of the adsorption-surface area plots at 1 and 48 hours are 1.3×10^{-6} and 2.2×10^{-6} moles Al_b/m^2, respectively. For those solutions in which there is a large excess of Al_b, about 40 percent of the adsorption occurs between 1 and 48 hours. A possible explanation for the longer time of completion of adsorption of Al_b is that the Al_b polymers, being larger and having less charge per aluminum atom than Al_a, are less mobile. Figure 17, the plot of adsorption of Al_b against the time of contact between the solutions and the surfaces, shows how quickly the adsorption does occur. Seemingly, it would completely stabilize after several days, thereby allowing us to account for Al_b polymerization as the sole process causing disappearance of Al_b after those several days. At 48 hours, the slope of Al_b adsorption, 2.2×10^{-6} moles/m^2, is considerably larger than the slope of Al_a adsorption at that time, 8.0×10^{-7} moles/m^2. This is in general agreement with many observations in the literature which report strong adsorption effects for polynuclear ions; however, the polynuclear species are generally large units, each containing many metal ions. Thus, each Al_b unit that is adsorbed has a much larger effect on analytically determined aluminum than does the adsorption of a single aluminum monomer.

The Al_b units represent a range of compositions, with a net charge per aluminum atom that probably is commonly less than one, and so an ion exchange equilibrium model probably cannot be expected to be appropriate for this kind of material. Also, the techniques used by

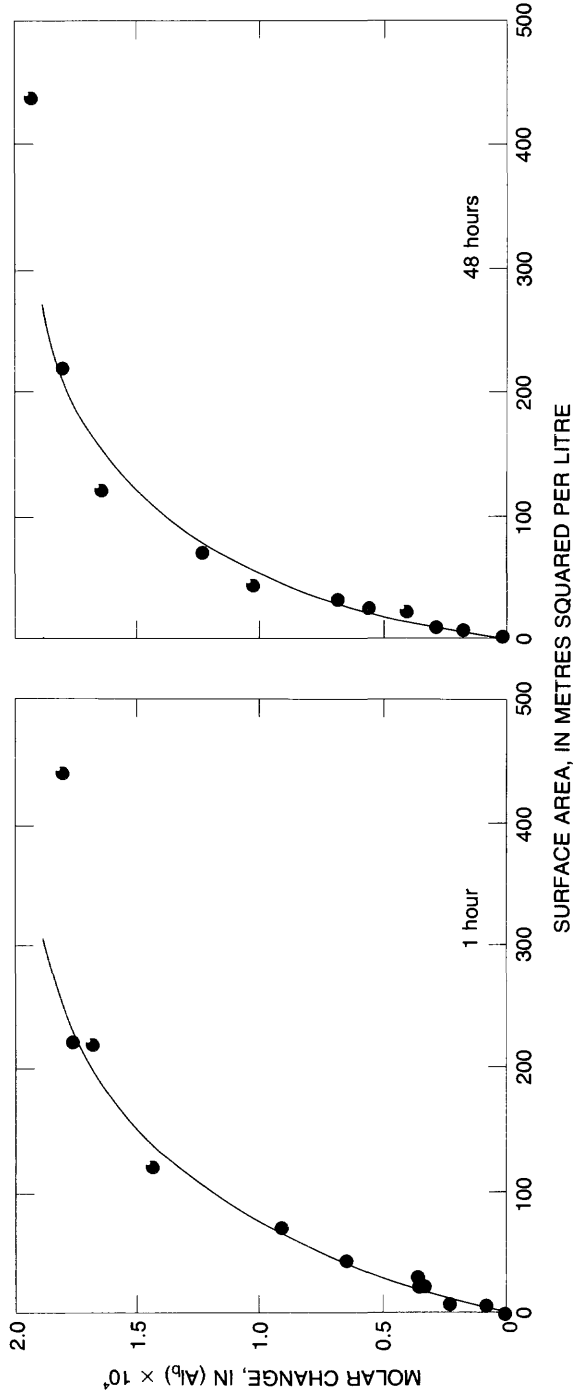

FIGURE 15.—Adsorption of Al_b at 1 hour and 48 hours in solutions DS as a function of effective area of surface added.

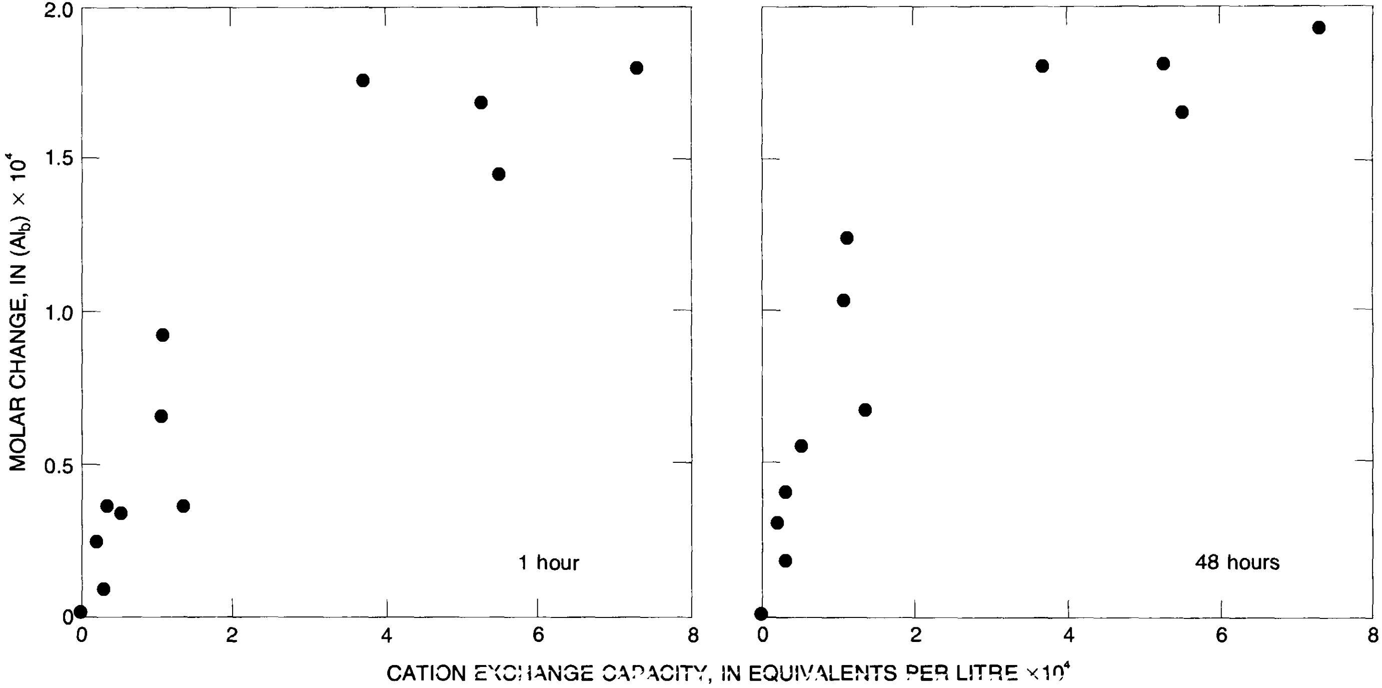

FIGURE 16.—Adsorption of Al_b at 1 hour and 48 hours in solutions DS as a function of cation exchange capacity.

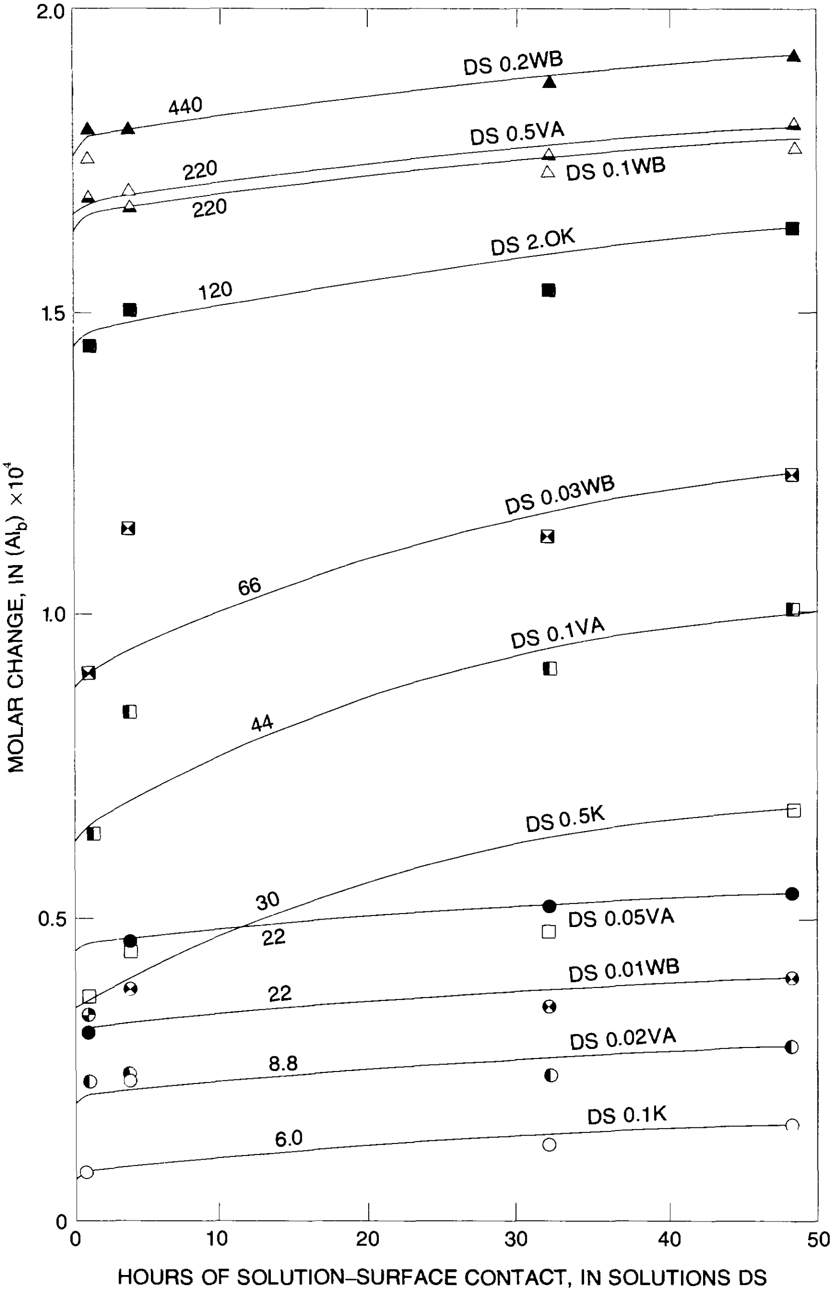

FIGURE 17.—Adsorption of Al_b as a function of contact time for different amounts and types of mineral surfaces. Effective surface area in metres squared per litre is noted for each solution.

Smith and Hem (1972) for estimating the size and charge of such species cannot be readily applied where the pH may not reflect correctly the increasing proportion of bridging hydroxide ions.

The apparent adsorption of Al_b can, however, be studied by other procedures. Nearly all adsorption of Al_a and most of that of Al_b took place during the first hour of contact between the surfaces and solutions. Furthermore, for many of the solutions, aqueous concentrations of Al_b also decreased between 1 and 48 hours. This effect is more pronounced for those solutions having the higher surface areas and is due to further adsorption by the surfaces or to an increased rate of polymerization of Al_b catalyzed by the surfaces, or to a combination of both. In order to study this effect more closely, first-order rate constants were computed where possible, for the disappearance of Al_b from the solutions during the period between 1 and 48 hours after preparation. Although there was a general tendency for a faster rate in solutions containing the greater amounts of surface, the relationship was not very well defined. Rates of disappearance of Al_b from comparable aging-study solutions during longer aging periods generally are slower than rates for the 1–48-hour aged solutions observed here, but this comparison could only be made in a small number of solutions. Where a substantial amount of Al_b was adsorbed before the first measurement, at 1 hour, the continuing loss of Al_b may have been attributable to continued adsorption rather than to polymerization. We cannot definitely conclude from comparison of these rates with surface areas that the effect of surface area is to increase the polymerization rate; however, if such an effect exists, it evidently is not great enough to be of major importance.

EQUILIBRIUM MODELS FOR ADSORPTION OF Al_b

The plots of adsorption of Al_b as a function of surface area clearly show that the adsorption per unit area of adsorbent approaches a limiting value as the surface area approaches zero. Kipling (1965) presented a form of the Langmuir adsorption isotherm that describes this type of behavior:

$$\frac{a}{a_\infty}=\frac{bc}{1+bc},$$

where a is the adsorption of solute per mass (or area) of adsorbent at aqueous solute concentration c. The limiting value of a at saturation is a_∞, and b is a constant. This equation may be rearranged as

$$\frac{a}{c}=a_\infty b-ba.$$

By plotting the quantity a/c as a function of a, a_∞ and b can be determined. The relationship should define a straight line of intercept $a_\infty b$ and slope $-b$. The quantity a represents the observed decrease in Al species concentration (ΔC) times sample volume (V) in litres divided by area of surface (A). The quantity c is the observed aluminum species concentration.

Data required for calculation of a are given in table 8 for the 48 hour observations for Al_b. The results are given in table 11. Figure 18 is a plot of the results.

TABLE 11.—*Data used for development of Langmuir isotherm for adsorption of* Al_b

Solution	A/V (m^2/1)	$C\times10^4$ (moles/litre)	$\Delta C\times10^4$ (moles/litre)	$\frac{\Delta C\times10^4}{A/V}$ (moles/m^2)	$\frac{\Delta C}{CA/V}$ (litres/m^2)
DS NAS	0.0	1.94	0.00	------	------
DS 0.01WB	22	1.54	.40	0.0182	0.0118
DS 0.03WB	66	.70	1.24	.0188	.0268
DS 0.1WB	220	.14	1.80	.0082	.0584
DS 0.2WB	440	.01	1.93	.0044	[1].438
DS 0.02VA	8.8	1.63	.30	.0341	.0209
DS 0.05VA	22	1.38	.56	.0254	.0184
DS 0.1VA	44	.92	1.02	.0232	.0252
DS 0.5VA	220	.13	1.81	.0082	.0633
DS 0.1K	6.0	1.77	.17	.0280	.0160
DS 0.5K	30	1.27	.67	.0224	.0176
DS 2.0K	120	.29	1.65	.0137	.0473

[1] The measurement of aqueous Al_b for solution DS 0.2WB gave a value at or below the detection limit (10^{-6} molar) and, therefore, is a very highly uncertain $\frac{\Delta C}{CA/V}$ value. Consequently, this point is not considered in determining slope and intercept.

From inspection of figure 18, it is seen that the adsorption of Al_b could be explained by the Langmuir isotherm. The results are used to determine a_∞ and b, which are found to be 3.7×10^{-6} moles/m^2 and 1.8×10^4 litres/mole, respectively. This says that at saturation, with an excess of Al_b remaining in solution, the surface would adsorb 3.7×10^{-6} moles Al_b per square metre of surface area, or one atom in Al_b per 45 square angstroms. Therefore, the maximum adsorption a_∞ corresponds to less than a monolayer for our Al_b polymeric ions. The derived adsorption coefficient, 3.7×10^{-6} moles Al_b/m^2, compares reasonably well with the observed adsorption of 2.2×10^{-6} moles Al_b/m^2 in the test solutions where concentrations were as much as 2×10^{-4} moles/litre.

From the foregoing discussion the following general conclusions are drawn:

1. Al_b is rapidly removed from solution by adsorption when mineral surfaces are introduced into a system containing aqueous polynuclear aluminum hydroxide ions.
2. The adsorption process is related to surface area of the mineral available, and the relationship follows the pattern of the Langmuir isotherm.

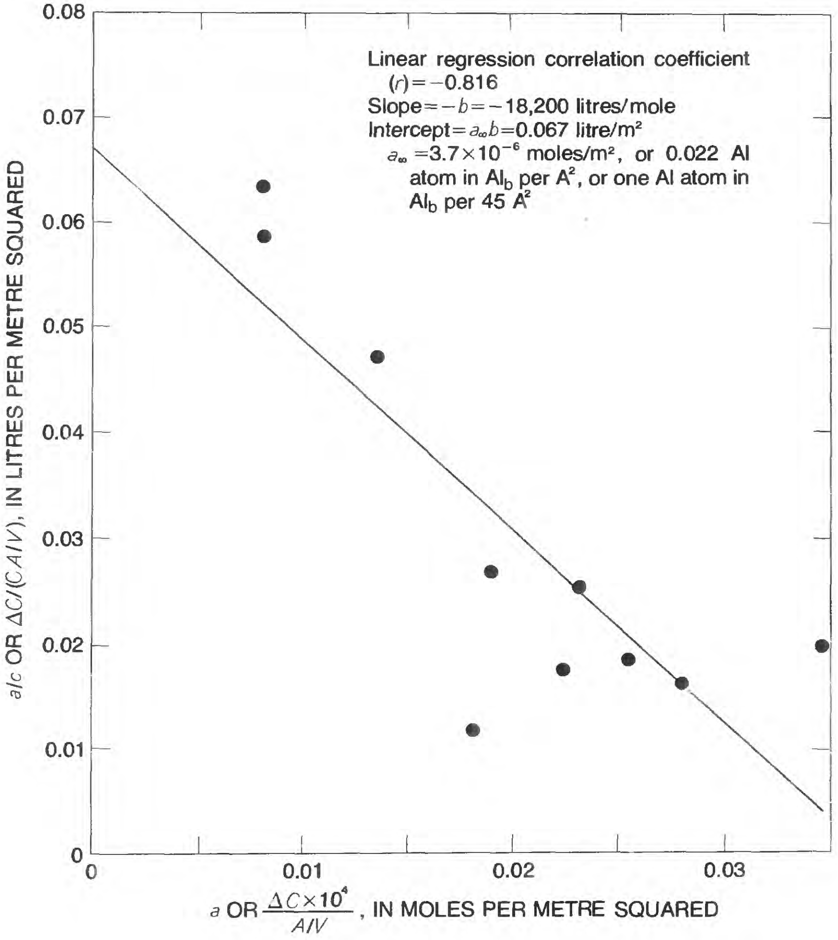

FIGURE 18.—Fit of Al_b adsorption at 48 hours to Langmuir isotherm parameters.

3. Polymerization of Al_b occurs in the solution at about the same rate whether a surface is present or not.
4. The initial take up of Al_b by the surfaces does not appear to involve extensive polymerization because the differences in pH between blank solutions and those having various amounts of surfaces are small compared with the difference in Al_b content. Polymerization to the extent required to account for Al_b conversion to Al_c should produce enough H^+ to materially affect the pH.

BEHAVIOR OF Al_c

As noted previously, aqueous Al_c cannot be directly determined from the available information. It can be calculated for solutions to which no mineral surface was added, and we know some Al_c was present at 48 hours in DS NAS (table 8). It seems reasonable that this material or its precursor also occurred in the other solutions before the mineral surfaces were added to them, but the development of recognizable crystallinity in this material is probably more rapid at the mineral surfaces. Because the change in solution pH is not large enough, it seems unlikely that very much of the Al_b that disappeared was fully converted to Al_c; however, the values for aqueous Al_c in table 8 were computed from the difference between determined Al_a+Al_b and the determined total aqueous aluminum and thus should be reasonably valid. The quantity of adsorbed Al_c given for the DS solutions in table 8 represents the difference between aqueous Al_c in solution DS NAS and in solutions with mineral surfaces. In any event, the assumptions and calculations involved probably give the numbers for Al_c sorbed a rather high degree of uncertainty; efforts to correlate adsorbed Al_c with surface area indicated only a rather tenuous relationship, and no quantitative treatment is presented here.

It is possible, however, by means of the electron microscope to detect the presence of Al_c at the mineral surfaces as gibbsite crystals, which can be discerned in the electron micrographs of solids recovered from these solutions after approximately 100 days (figs. 19–21). The hex-

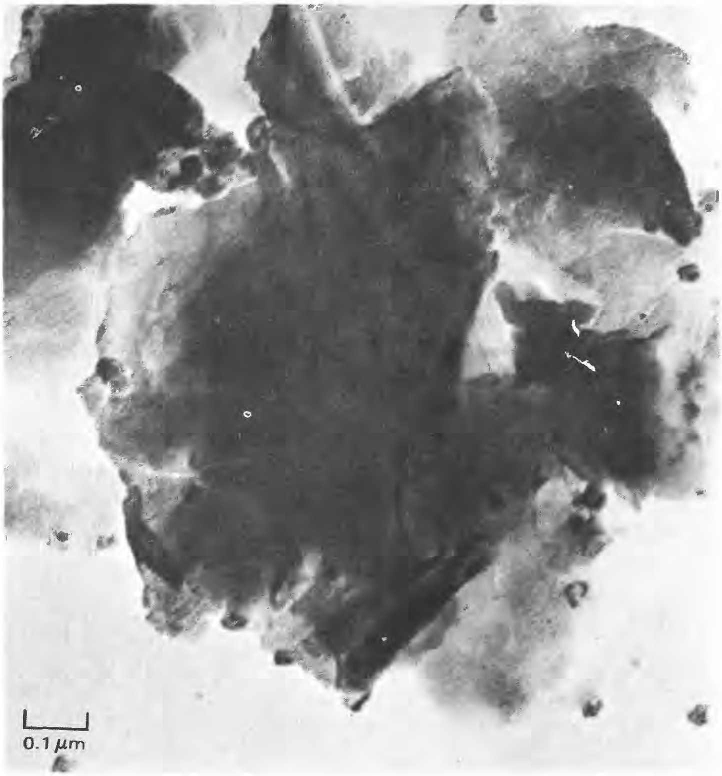

FIGURE 19.—Gibbsite crystallization centers on Wyoming bentonite after 100 days aging.

FIGURE 20.—Gibbsite crystals on surface of volcanic ash fragments after 100 days aging.

agonal plates adhere to the other mineral surfaces. Some of these crystals may have grown through polymerization of adsorbed Al_b, but direct sorption of the small crystals that had developed in the solution also has probably occurred. In solutions without surfaces that have been aged for a comparable length of time, one would be able to find similar gibbsite crystals that had developed independently.

Figure 22 shows a few gibbsite platelets on the surfaces of kaolinite removed from solution DS after 48 hours of aging. No crystals of gibbsite could be found in solutions without surfaces at this pH range in any of our previous work until after a longer aging period. Thus, the surfaces may facilitate the development of crystalline gibbsite, but as indicated by other evidence previously cited, the principal effect of the surfaces is that of adsorption.

EFFECTS OF SURFACES ON APPROACH TO EQUILIBRIUM

In previous work the solutions were assumed to have reached a state of equilibrium when the Al_b had all disappeared, by conversion to Al_c.

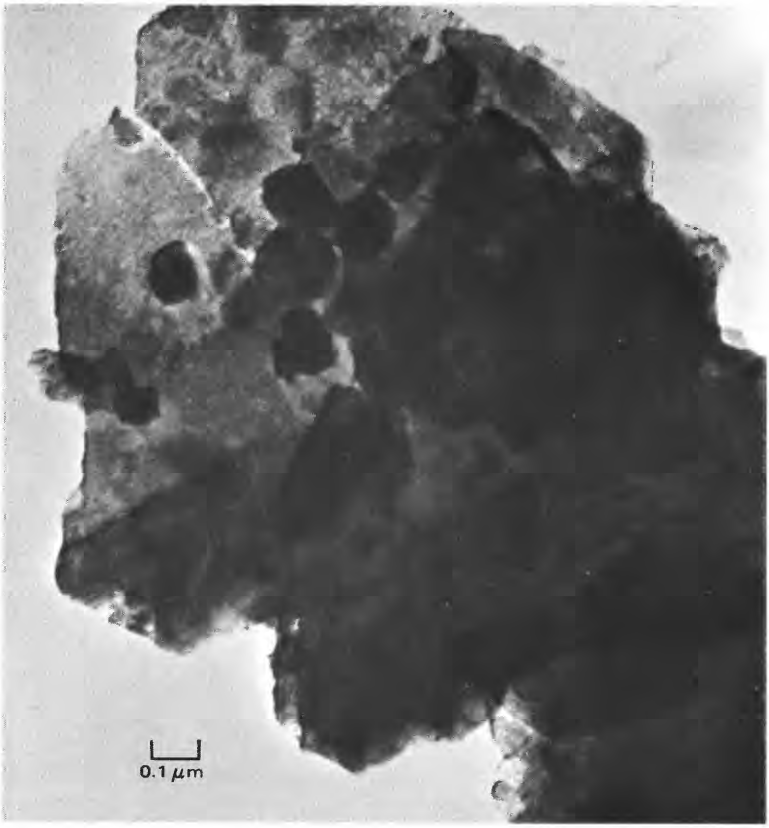

FIGURE 21.—Gibbsite crystals on surface of kaolinite after 100 days aging.

After that time, the pH remained constant. When the mineral surfaces were added, a substantial loss of dissolved aluminum commonly ensued, although it appeared generally not to be accompanied by a change in pH that was as large as would be expected were the process a polymerization of Al_b.

The approach to equilibrium in the absence of surfaces was traceable by the decreasing pH. Actual changes in Al_a, although generally small, were observed in these solutions, probably because they had initially larger amounts of Al_b than previously studied solutions where Al_a remained nearly constant. In any event, the surfaces did help speed the attainment of equilibrium by adsorbing nonequilibrium species, where this was all that was needed to attain equilibrium. Where more extensive changes in solution composition were needed to attain equilibrium, the surfaces may not always promote such changes and could even inhibit them. However, the latter effect is probably rather rare.

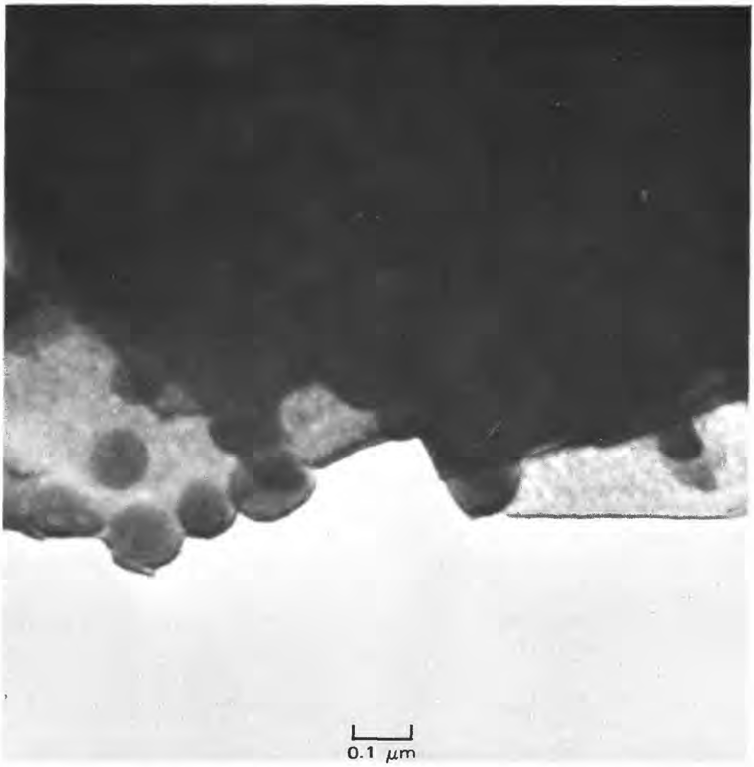

FIGURE 22.—Gibbsite platelets on surface of kaolinite after 48 hours aging.

CONCLUSIONS REGARDING SORPTION AND POLYMERIZATION EFFECTS

When a solution that is supersaturated with respect to gibbsite comes in contact with mineral surfaces having CEC, the experiments performed here suggest that a rapid decrease in dissolved aluminum species concentration occurs. The changes in concentration are most extensive during the first hour of reaction time and are closely correlated with effective surface area or CEC per unit volume of solution.

The weight of experimental evidence suggests that the aluminum species are removed by adsorption and that the adsorbed material does not undergo rapid polymerization to crystalline gibbsite. There may be some hydrolysis of monomeric dissolved aluminum species at the surface to increase the amount of hydroxide bound to aluminum, and microcrystals of gibbsite may be sorbed by the surfaces.

Surfaces used in these studies had some relatively subtle effects on distributions of dissolved species and rates of equilibration. However, after the initial adsorptive phase of the reactions was completed, the continued polymerization of the remaining Al_b proceeded at the same rate and probably by the same mechanism as observed previously in solutions that had no added surface.

It should be noted that because surfaces were added after the initial mixing of Al^{+3} and OH^-, the experiments do not permit evaluating the effect surfaces might have had on the initial formation of Al_b. Also, the pH range of the solutions was relatively narrow and was too low to include systems in which $Al(OH)_4^-$ would have been a significant constituent. However, the results do indicate that the adsorption process can have significant effects on the behavior of aluminum in natural systems.

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