CLAY MINERAL SYNTHESIS — III
RAPID HYDROTHERMAL CRYSTALLIZATION
OF AN ALUMINIAN SMECTITE

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Abstract — An aluminian smectite with about one Al^{3+}/Si^{4+} replacement per unit cell was batch-synthesized on a large scale (100-gal autoclave) at 300°C and 1240 psig with reaction times of several hours rather than days. This rapid crystallization was related to the use of NH_4^+ as the charge-balancing cation and to partial F/OH substitution. The short synthesis time prompted a study of continuous crystallization. Either of two techniques, flow through a stirred autoclave and through a multi-staged reactor column, produced crystalline product; neither gave the crystallinity of the batch process.

INTRODUCTION

AN EARLIER paper in this series (II. Granquist and Pollack, 1967; see also, Granquist, 1966) described the hydrothermal synthesis of a randomly-interstratified dioctahedral 2:1 layer silicate, which contained only Al^{3+} in octahedral sites. Charge imbalance caused by tetrahedral substitution of Si^{4+} by Al^{3+} (about one replacement per unit cell) was compensated by Na^+, which was present during synthesis. Necessary reaction times were in the range 1–2 days.

The present writing details: (1) a large-scale (100 gal autoclave) preparation, in a reaction time of several hours, of a similar layer silicate with NH_4^+ as the charge balancing cation, and with partial F/OH substitution; and (2) continuous crystallization of an aluminian smectite by flow through the 100–gal stirred autoclave and by flow through a multi-stage stirred reactor column designed for this application. Neither of the continuous methods gave the crystallinity of a properly operated batch process.

Wright *et al.* (1972) have discussed in detail the structure and properties of a batch product which differed from the synthetic mineral of this paper only in the degree of tetrahedral substitution. They described a hydrated randomly interstratified assemblage of mica-like (10·4 Å) and montmorillonite-like (12·5 Å) layers; the fraction of mica-like layers was $\frac{2}{3}$. The non-integral 00*l* sequence characteristic of the interstratified stacking collapsed to an integral sequence with $d_{001} = 9·4$ Å upon calcination at 650°C for 3 hr in air. The batch product of this paper behaved in the same way, except that the fraction of mica-like layers was very nearly $\frac{1}{2}$. Since the synthetic mineral has

been adequately described by the above authors, and by Granquist (1966) and Granquist and Pollack (1967), this paper will deal primarily with the synthesis details.

In like manner, discussion of continuous synthesis will concentrate on the operational detail. The product was similar to that produced by the batch method, but contained considerable boehmite and amorphous silica.

EXPERIMENTAL

Batch operation

Silicic acid sol, assaying 5·2% SiO_2, was prepared by ion-exchange of sodium silicate solution (Philadelphia Quartz Company N-grade, added to water) over a hydrogen exchange resin. Sufficient gibbsite, as commercial alumina trihydrate (Alcoa C-31), was added to this sol, with agitation, to bring the Si/Al ratio to 1·4 (equivalent to about one Al/Si replacement per unit cell). The resulting slurry was charged to a 100-gal jacketed, stirred autoclave, the proper amounts of NH_4F and NH_4-OH added to provide an NH_4/Al ratio of 0·2 and a F/Si = 0·1, and the autoclave heated (Dowtherm with electrical immersion heaters). Samples were drawn from the system and quenched at various times during the heat-up and isothermal (300°C) parts of the run. Figure 1 shows the observed temperature-time relationship and the various sampling points.

The procedure was repeated with the NH_4F/NH_4OH replaced by equivalent amounts of (1) NaF/NaOH, (2) NaOH (similar to Granquist and Pollack, 1967), and (3) NH_4OH. The several samples were dried at 105°C, ground and studied by X-ray diffraction.
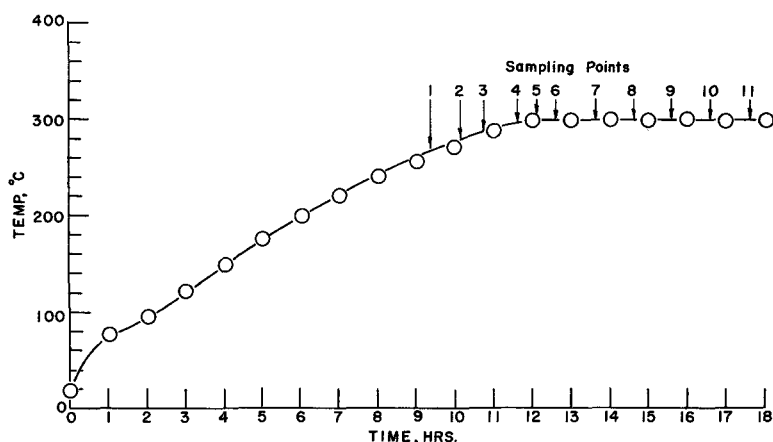
Fig. 1. Heating curve for 100-gal autoclave. Some typical sampling points are indicated.

Continuous operation

The feed slurry was prepared by the method described above for the NH_4F/NH_4OH batch experiment.

Autoclave. The apparatus consisted of a 100-gal stirred autoclave, a Manton-Gaulin high pressure feed pump, a condenser for quenching the product slurry removed from the autoclave by a dip-tube, and a control valve for dropping the product slurry from synthesis pressure (1240 psig) to atmospheric pressure. The feed-rate was controlled by recycling part of the output of the fixed stroke pump to keep the heat demand within the BTU capability of the autoclave. The volume in the autoclave was kept reasonably constant by adjusting the discharge rate to maintain balance between the volume introduced and the volume removed. When steady-state conditions were obtained (see later discussion), product was collected, dried, and studied for crystallinity.

Staged reactor. A special vessel (see Fig. 5) was designed (RCB) for this experiment. The feed slurry was pumped to the vessel by a variable-stroke 4-cylinder Hills-McCanna feed pump, with each cylinder operating 90° out-of-phase to minimize flow variations. A preheater, consisting of a coil immersed in electrically heated Dowtherm, was placed in line between the feed pump and the reactor.

The output of the vessel was controlled by an air-operated Fisher controller operating an air-activated throttling valve. Two such valves and controllers were connected in parallel, with one valve doubling as stand-by and, with a set point higher than normal operating pressure, as a safety device. The operating pressure was kept about 100 psi higher than the vapor pressure of water at

the maximum reactor temperature (1240 psig). A water cooled quench condenser was located between the reactor and the throttling valve. The heaters were arranged in four separately controlled sections along the length of the reactor. The total assembly permitted flow up or down the column at various rates, controlled temperature gradients along the column, and varying pressures above those equivalent to the operating temperature.

RESULTS AND DISCUSSION

Batch operation

X-ray examination of the various samples followed the procedures described by Granquist and Pollack (1967) and Wright, Granquist, and Kennedy (1972). Diffractometer traces (CuK_α radiation), obtained from the NH_4F/NH_4OH synthesis at $T = 270°C$ and at $T = 300°C$, $t = 0$ hr (i.e. just as the autoclave contents reached the desired reaction temperature, point 4 in Fig. 1), and from the NaF/NaOH synthesis at $T = 300°C$, $t = 0$ hr, appear in Fig. 2. The development of the 06 reflection for samples taken from the $NH_4F/NHOH$ and NaF/NaOH systems, is shown in Fig. 3. The basis for the relative intensities was the 300°C, 2 hr. sample from the NH_4F/NH_4OH system. For the synthesis in the presence of NaOH and NH_4OH (i.e. no fluoride), the 06 could not be detected even after 12 hr at 300°C.

Thus the use of fluoride ion, proxying for hydroxyl, markedly increased the rate of crystallization. Replacement of Na by NH_4 contributed a further increase.

The superiority of NH_4^+ over Na^+ is at least partly explained by Fig. 4, a collection of X-ray diffractometer traces covering the range $12–24°2\theta$.
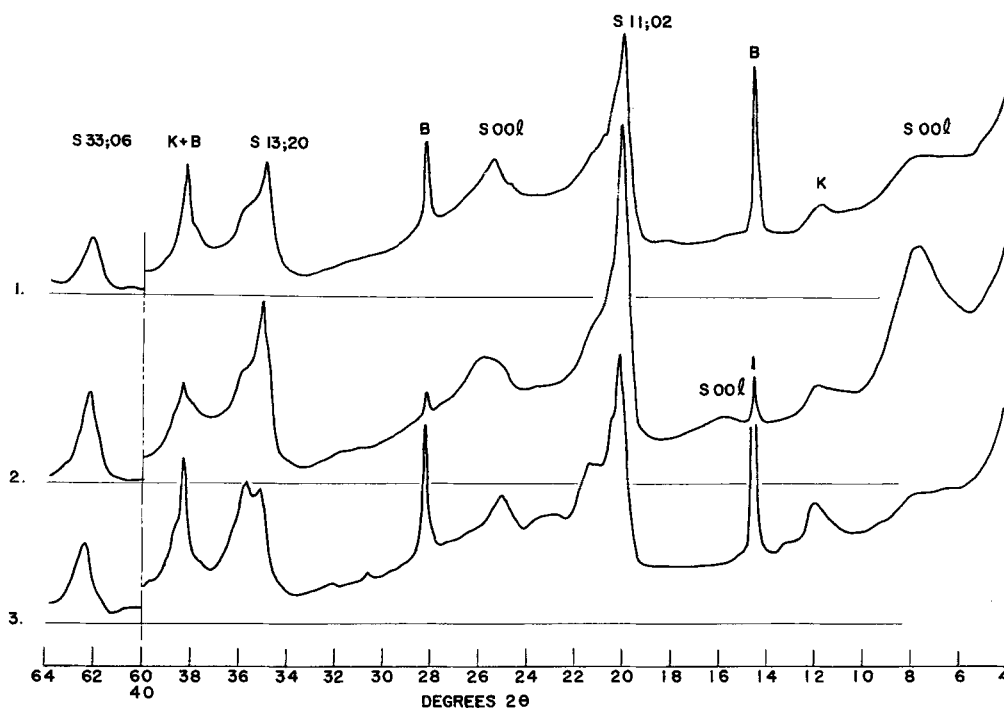
Fig. 2. Diffractometer traces (CuK$_\alpha$ radiation). NH$_4$F/NH$_4$OH synthesis: Curve 1, sample withdrawn at 270°C (pt. 1 in Fig. 1) and quenched; Curve 2, sample withdrawn at 300°C (pt. 4 in Fig. 1). NaF/NaOH synthesis: Curve 3, sample withdrawn at 300°C (pt. 4 in Fig. 1) and quenched.
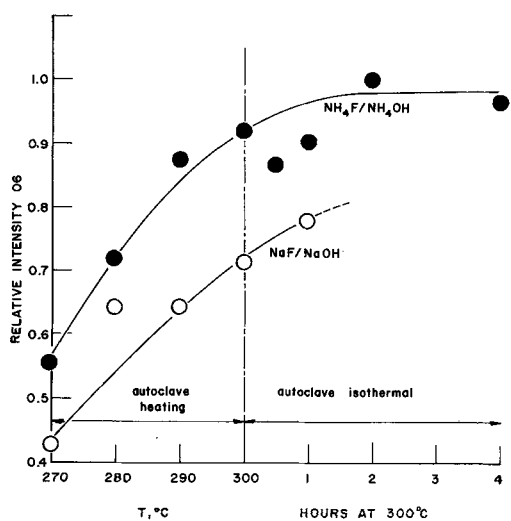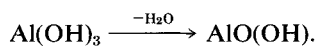

Fig. 3. Relative intensity of 06 reflections as a function of synthesis time/temperature. Comparison of the effects of Na and NH$_4$.

It is apparent that Na$^+$ promoted the hydrothermal dehydration of gibbsite to boehmite.

$$Al(OH)_3 \xrightarrow{-H_2O} AlO(OH).$$

Boehmite has proved to be slowly reactive, presumably because of unsuitable solubility under the experimental conditions. Thus, the Na$^+$-promoted gibbsite–boehmite conversion caused a decrease in the overall rate of crystallization of the desired smectite.

gibbsite $\xrightarrow{\text{fast}}$ smectite

fast   slow

boehmite
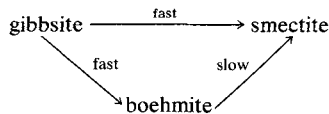
It is more difficult to account for the mineralizing action of the fluoride ion. The F/OH ratio probably controlled the relative solubilities of Al^{3+} and Si^{4+} by pH adjustment and complex formation. The intriguing possibility also exists that part of the effect may have been entropic in origin. That is, as the crystal nucleated and grew, the isotropic
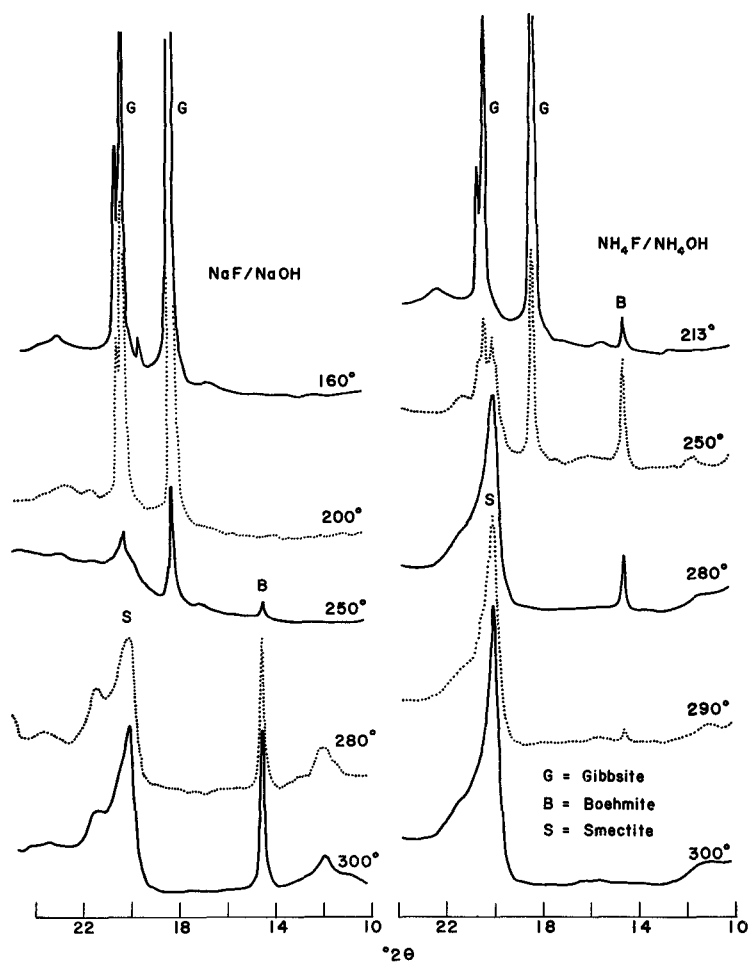
Fig. 4. Development of the silicate 11;02 reflection at ~4·46 Å (20°2θ). Comparison of the effects of Na$^+$ and NH$_4^+$.

F$^-$ ion could enter its structural site more readily than the anisotropic OH$^-$ ion, which must have entered the same site with a particular orientation.

Continuous operation

Autoclave. With the assumptions of instant, perfect stirring, and a constant operating volume (i.e. rate of feed equals rate of discharge), the replacement of the initial ($t = 0$) volume V_o by added material in some time t is

$$\theta = 1 - e^{-t/\tau}. \tag{1}$$

The symbols have the following meaning: θ is the fraction of the "holding-volume" V_o replaced in time t; $\tau = V_o/k =$ average residence time, where k is the feed rate. The ratio t/τ is dimensionless. For

this experiment, it was assumed that steady-state conditions had been reached at $\theta = 0.9$, which corresponds approximately to $t/\tau = 2.5$.

R. J. White (personal communication) continued this analysis to provide the distribution of product ages as a function of τ. Fig. 6 demonstrates that optimum operation should be obtained in the range of $\tau = 1.2$–2.0 hr.

A typical result was obtained at $V_o = 50$ gal and $k = 12$ gal/hr. Under these circumstances, $\tau = 4$, a value greater than optimum but prescribed by the maximum heat transfer obtainable. The run started with water in the autoclave at 300°C and 1240 psig. The volume in the autoclave was held near 50 gal by balancing volume in and volume out. Small samples were collected periodically and solids content determined to check equation (1). With

Mixing Equipment Co. Type NLDG–75V
Variable Mixer Drive Mounted to
Top Flange.
Speed Range: $\frac{525}{175}$ rpm.

Cooley "Thermoshell"
Electric Heaters

Insulation

All Wetted Surfaces, 316 S.S.
Vessel I.D.: 5.76 inches
Total Vol.: 1515 cu. in.
6.56 gal.
Working Pressure: 1400 psi.
Working Temp.: 300°C
572°F
Shaft Diam.: $\frac{1}{2}$ inch
Horizontal Baffle
Shaft Opening Diam.: $\frac{9}{16}$ inch

Vertical Baffles

Horizontal Baffles

Openings for Inlet, Discharge,
Sampling & Thermocouple Wells
Made from $\frac{1}{4}$" O.D. Tubing &
Tube Connectors as Shown.
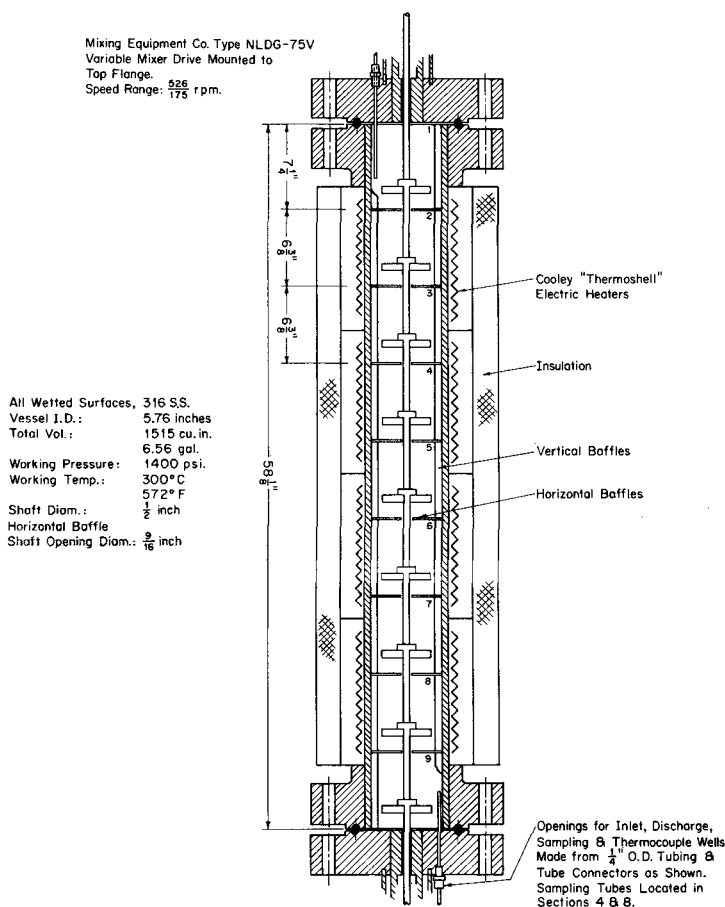Sampling Tubes Located in
Sections 4 & 8.

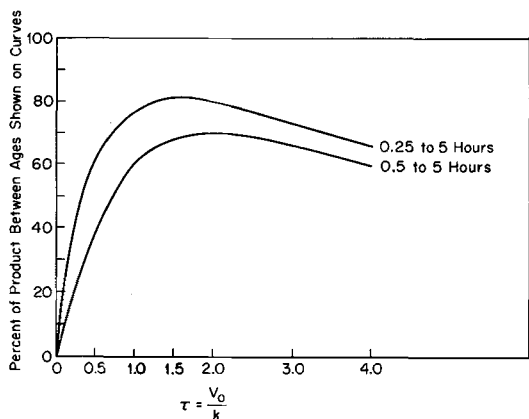Fig. 5. General layout of high pressure, continuous flow-through staged reactor column.

Fig. 6. Percent of product between ages shown on curves
as a function of τ, the holding time.

water initially present, the solids content at t should equal 100θ. The maximum deviation between theoretical and observed values for the solids content was less than 10%.

At $t = 10$ hr ($t/\tau = 2\cdot5$) product sample collection was started and continued for 1 hr (i.e. the product sample corresponded to the time interval $t = 10–11$ hr). The product slurry was dried and examined for crystallinity. The X-ray diffractometer trace is shown in Fig. 7.

The product from this type of continuous operation was a well-crystallized smectite mixed with unreacted feed components. The word "unreacted" is used loosely; actually, the alumina had been hydrothermally dehydrated from gibbsite to boehmite. This contamination by the feed was expected because the mathematical analysis showed that even under optimum conditions the product would
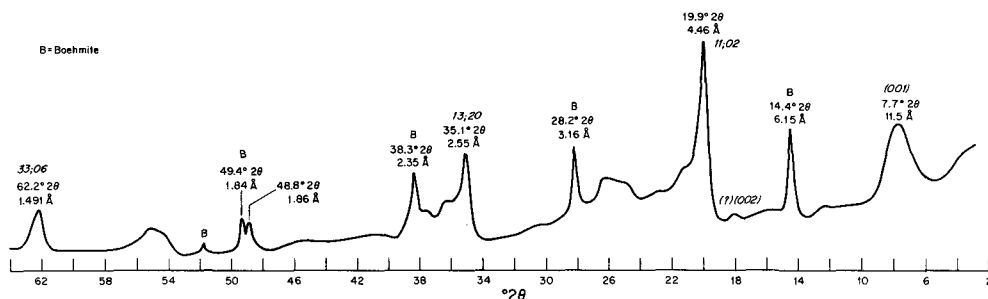
Fig. 7. X-ray (CuK$_\alpha$) diffractometer trace from continuous run. B — boehmite.

contain 20–25 per cent of material which had been in the reactor less than 0·5 hr.

Staged reactor. The working volume of this vessel was approximately 6 gal; i.e. total volume of 6·56 gal less the volume of shaft, agitators, baffles and head space. A typical run involved a feedrate of 2·5 gal/hr and thus a residence time of 2·4 hr. For the particular experiment described, flow was up the column and the temperature in each section was controlled at 300°C. Figure 8, a sequence of

diffractometer traces, serves as a good summary of the reactor performance.

Comparison of Figs. 8a with 8b shows the effect of passage of the feed slurry through the preheater and through section 9 of the column. During this stage the feed was heated from about 60°C at the slurry reservoir to about 220°–230°C at the exit of the preheater and then to about 300°C during flow through section 9. The X-ray patterns show that this operation caused a small amount of hydro-
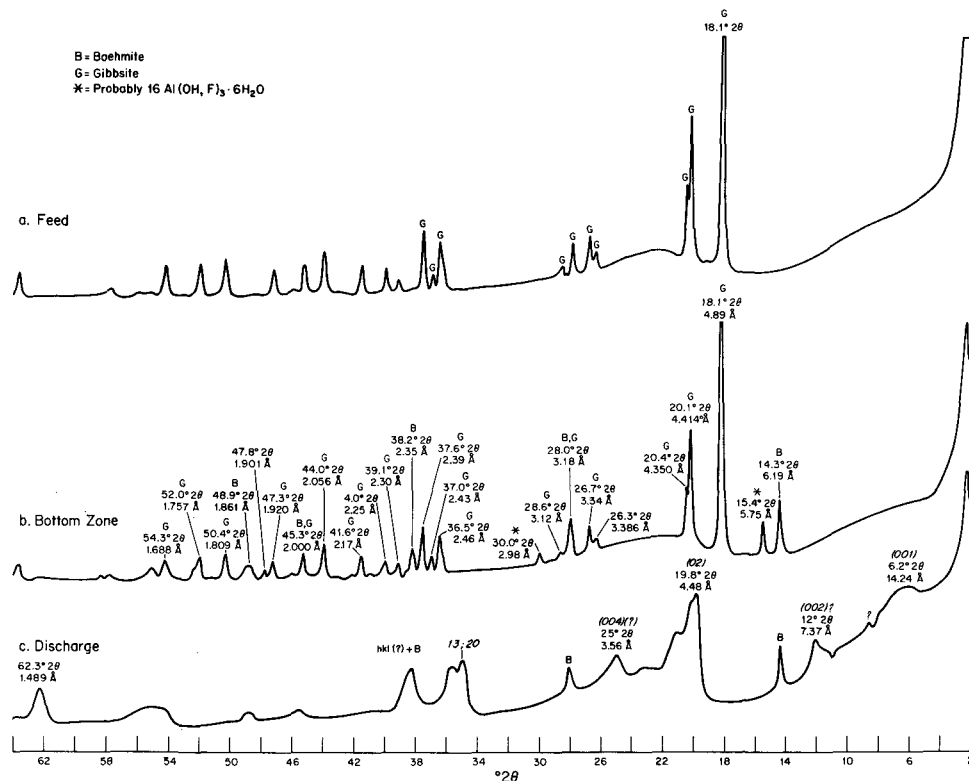

Fig. 8. X-ray (CuK$_\alpha$) traces of material from sequence of stages in flow reactor. B — Boehmite; G — gibbsite.

thermal dehydration of gibbsite to boehmite and the crystallization of a small amount of a compound which is probably $16 \, Al(OH,F)_3 \cdot 6H_2O$. With the exception of the peaks due to these compounds, 8a is similar to 8b.

Comparison of Figs. 8b with c illustrates the result of travel through the rest of the column. Note that no trace of the gibbsite peak at $4 \cdot 89$ Å remains; the strongest boehmite line at $6 \cdot 19$ Å is less intense in 8c than in 8b; the lines due to $16 \, Al(OH,F)_3 \cdot 6H_2O$ have disappeared; and the product is well-crystallized in the a–b plane, but poorly organized in the c-direction. The product was judged well-crystallized by the absence, with the exception of a small amount of boehmite, of crystalline alumina phases, and the intensity of the $11;02$, $13;20$, and $33;06$ reflections. The statement that the organization in the c-direction was poor is based on the broad low-intensity (001) reflection. Local (00l) order over sequences of several platelets (i.e. mica-like assemblies) must occur, however, for the (hkl) reflections to appear.

SUMMARY

By proper control of the ionic environment, an aluminian dioctahedral 2:1 layer silicate can be batch crystallized at 300°C in reaction times of several hours. A similar product can be synthesized continuously in either a standard batch-type autoclave adapted to continuous flow, or in a specially designed staged-reactor. Extension of these results to other 2:1 (and perhaps 1:1) silicates should be straightforward.

REFERENCES

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Résumé – Une smectite alumineuse contenant environ un remplacement Al^{3+}/Si^{4+} par maille a été synthétisée à grande échelle par un processus de lit mobile (autoclave de 100 gal) à 300°C et 1240 psig en nécessitant des temps de réaction de plusieurs heures au lieu de plusieurs jours. Cette cristallisation rapide a été reliée à l'utilisation de NH_4^+ comme cation compensateur et à une substitution partielle F/OH. Le temps de synthèse qui est court incite à étudier la cristallisation continue. Chacune des deux techniques suivantes, écoulement à travers un autoclave avec agitation et écoulement à travers un réacteur colonne à plusieurs étages, fournit un produit cristallin; aucune des deux ne donne la cristallinité du processus à lit mobile.

Kurzreferat – Ein Aluminium–Smectit mit etwa einem Al^{3+}/Si^{4+} Ersatz pro Einheitszelle wurde chargenmässig im Grossmaszstab (100 Gallonen Autoklav) bei 300°C und 1240 psig, mit Reaktionszeiten von einigen Stunden eher als Tagen, synthetisiert. Diese rapide Kristallisation stand in Beziehung zu der Verwendung von NH_4^+ als dem ladungsausgleichenden Kation und zu teilweisem F/OH Austausch. Die kurze Synthese veranlasste zu einer Studie kontinuierlicher Kristallisation. Jede der beiden Methoden: Strömung durch einen Rührautoklaven sowie durch eine mehrstufige Reaktorkolonne, lieferte ein kristallines Produkt. Keine ergab die Kristallinität des Chargenprozesses.

Резюме — Порция алюмомонтмориллонитовой глины с приблизительно одним Al^{3+}/Si^{4+} обменом на единицу ячейки синтезировалась в крупногабаритном автоклаве емкостью 100 галлонов при температуре 300°C и давлении 1240 фунт/дюйм² со временем реакции несколько часов, а не дней. Эта быстрая кристаллизация произошла благодаря использованию NH_4^+ в качестве балансирующего загрузку катиона и благодаря частичному замещению F/OH. Короткое время синтезирования повело к изучению непрерывной кристаллизации. По любому из этих методов, пропуску через перемешиваемый автоклав или через многоступенчатую реакционную колонну, получили кристаллический продукт, но ни тот ни другой метод не дали кристалличности периодического процесса.