

CHLORITIZATION OF MONTMORILLONITE BY ITS COPRECIPITATION WITH MAGNESIUM HYDROXIDE

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Abstract—A magnesium hydroxide-montmorillonite complex prepared at an OH/Mg molar ratio of 2 (16 meq Mg/g clay) and immediately cleaned of any free $Mg(OH)_2$ behaves like magnesium-chlorite and shows no change during 3 months ageing. Magnesium hydroxide completely precipitates within the interlayer space of montmorillonite. X-ray diffraction analysis, thermal (DTA and TGA) studies, i.r. absorption analysis, polarographic reduction behaviour, and cation exchange capacity measurements confirm the transformation of montmorillonite to a chlorite-like structure. Further ageing of the complex results in the release of brucite from the interlayer space and expansion of the complex on glycerol treatment. X-ray analysis of the 6 months aged sample shows the presence of free brucite but not montmorillonite. A small but significant increase in CEC of the complex is observed on ageing. When the $Mg(OH)_2$ -montmorillonite complex is allowed to age in the presence of free $Mg(OH)_2$ (external to montmorillonite unit layers) in a dry state, a "seeding" effect takes place and the "fixed" $Mg(OH)_2$ starts coming out from the interlayer space after 10 days.

INTRODUCTION

THE FACT that chlorites result from the alteration of biotite, hornblende, and other minerals has led to laboratory studies of chloritization of expansible layer silicates, mainly by the coprecipitation of metal hydrous oxides and expansible silicates like montmorillonite and vermiculite (Rich, 1968). Different metals (hydrous oxides) have been used for this purpose and in recent years data has accumulated on the preparation and characterization of hydroxy aluminum-montmorillonite complexes (Barnishel and Rich, 1963; Brydon and Kodama, 1966; de Villiers and Jackson, 1967; Gupta and Malik, 1969; Hsu, 1968; Hsu and Bates, 1964; Kawaski and Aomine, 1965; Rich, 1968; and Turner and Brydon, 1967).

Caillere and Henin (1949) were the first to study the $Mg(OH)_2$ -montmorillonite complex. Slaughter and Milne (1960) obtained chlorite like structures from montmorillonite, by its coprecipitation with $Mg(OH)_2$ and $Al(OH)_3$, and have stressed the "contrast in chemical conditions of precipitation and the properties of the hydroxide precipitates".

The OH/cation ratio and pH (Barnishel and Rich, 1963; Brydon and Kodoma, 1966; Hsu and Bates, 1964; Kawaski and Aomine, 1965; Rich, 1968; Slaughter and Milne, 1960; Turner and Brydon, 1967; and Wiesmiller *et al.*, 1967) are

important factors in these studies. Barnishel and Rich (1963) found that only at an OH/Al ratio of 1.5 or less were the aluminum interlayers stable in $Al(OH)_3$ -montmorillonite complexes. Rich (1968) has discussed some stable interlayers obtained at an OH/Al ratio of 3.27. The interlayers formed in neutral or alkaline pH range are less stable in comparison to those obtained in acidic pH range. However, the precipitation of $Mg(OH)_2$ takes place in an highly alkaline pH range as compared to the precipitation of $Al(OH)_3$. It was, therefore, thought worthwhile to study the $Mg(OH)_2$ -montmorillonite complex obtained in an alkaline pH range. Experiments have been conducted, both in the presence and absence of free metal hydroxide (external to montmorillonite unit layers), to study the effect of free metal hydroxide on the removal of interlayer hydroxide.

MATERIALS AND METHODS

Montmorillonite. The 2-0.2 μ fraction of montmorillonite (supplied by British Drug House) was obtained from a water dispersed system. No other preliminary treatment (or cation saturation) was given; as in similar studies (Barnishel and Rich, 1963; Slaughter and Milne, 1960) the absence of homo-ionic saturation has been stressed. The clay contained no organic matter. A 6 g portion of the clay was suspended in distilled water for each treatment.

Precipitation of $Mg(OH)_2$. $Mg(Cl)_2$ (Analytical

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Grade) was added to the montmorillonite suspension to give a 2N solution. The suspension was then neutralized by a controlled dropwise addition of 200 ml of normal NaOH at the rate of 1 ml per 5 min, while stirring continuously at a high speed with a magnetic stirrer (approximately 2000 rev/min). This precipitated about 200 meq of $\text{Mg}(\text{OH})_2$ per 6 g montmorillonite at an OH/Mg molar ratio of 2.0 in about 17 hr. The precipitation was conducted in triplicate. Similar precipitations were also performed in solutions of $\text{Mg}(\text{Cl})_2$ only without adding the montmorillonite.

Mg(OH)₂-montmorillonite complex (system I). The precipitate was filtered, washed with a 1:1 alcohol-water mixture until free from chloride ions and dried at 105°C. The only cations that could be detected in the filtrate were Na^+ ions.

Acid washed Mg(OH)₂-montmorillonite complex (system II). For the second set of experiments, after precipitation the complex was mixed immediately with 0.05 N HCl (preliminary experiments were first conducted to estimate its quantity for dissolving only the free $\text{Mg}(\text{OH})_2$ external to montmorillonite unit layers), stirred for 10 min and filtered. The precipitate was leached with HCl until no more magnesium ions appeared in the filtrate. After washing the residue with alcohol-water mixture it was dried at 105°C.

Storage. The complexes were stored, between analysis, in desiccators containing anhydrous calcium chloride.

pH-measurement. The pH was measured with a Cambridge Bench Type pH meter using a glass calomel electrode assembly.

Cation exchange capacity. CEC was determined by a number of different methods, viz. analytical (ammonium acetate leaching), flame photometric, polarographic, and potentiometric and conductimetric titrations both in aqueous and alcohol media (Malik and Gupta, 1968a). Results of only the analytical method are given here.

Exchangeable magnesium. Exchangeable magnesium was determined by displacing magnesium ions from a 2 g sample of $\text{Mg}(\text{OH})_2$ -montmorillonite complex with four washes, each consisting of 25 ml of normal NaCl. Magnesium was estimated, wherever required, by EDTA titrations and as pyrophosphate.

X-ray diffraction. Patterns were obtained on powder specimens (minus 300 British Standard Sieve) with a Philips 1051 PW Diffractometer, using a copper target with a nickel filter, at 26 KeV and 10 mA. Different combinations of the beam, Soller and detector slits at a scan speed of 0.2°/min were used to provide greater precision in determining the 2θ values.

I.R. analysis. I.r. spectra were obtained with

a Perkin Elmer Spectrophotometer No. 021 with "Nujol" mull specimens.

Charge determination. Migration of $\text{Mg}(\text{OH})_2$ -montmorillonite complex colloidal particles, under the influence of an applied emf, was observed in a Burton type electrophoresis apparatus.

RESULTS AND DISCUSSION

Montmorillonite. Exchangeable cation analysis by flame-photometric method showed the presence of sodium and calcium ions only in the montmorillonite. X-ray diffraction data of the montmorillonite used are comparable to that reported in Card no. 3-0019 (ASTM, X-ray Powder Data File, 1962). On treatment with glycerol, the 001 spacing expands to 17.7 Å, whereas on heating (600°C, 2 hr) it collapses to 9.3 Å.

MgCl₂-NaOH system. Immediately after precipitation the pH of the mixture was 11.2. No magnesium could be detected in the filtrate. The dry precipitate contained 41.5% Mg, equivalent to the composition $\text{Mg}(\text{OH})_2$. Even the freshly prepared product was crystalline to X-ray diffraction analysis, and the data are comparable to that reported in Card no. 7-239. No change in its pattern was observed with time. No chloride ions could be detected adsorbed on the precipitate. The product was soluble (100 per cent) in normal HCl (on boiling). After heating (600°C, 2 hr) $\text{Mg}(\text{OH})_2$ changed to MgO.

Mg(OH)₂-montmorillonite complex (Acid washed, system I). The pH of the montmorillonite suspension was 5.1; after $\text{Mg}(\text{OH})_2$ precipitation it rose to 10.8. Sodium ions were the only cations in the filtrate after precipitation, indicating that magnesium was completely precipitated and the original exchangeable cations of the montmorillonite were either not displaced at all or accommodated elsewhere in the new product formed, as has also been observed earlier (Slaughter and Milne, 1960).

Following precipitation the washed and dried product was crystalline to X-ray diffraction analysis, supporting the earlier data (Slaughter and Milne, 1960) that new structures develop upon association of the unit layers through dehydration. It differs from the hydroxy aluminum-montmorillonite complex (Gupta and Malik, 1969) which remained amorphous for 10 hr after drying. The presence of peaks for brucite (Table 1) along with those of $\text{Mg}(\text{OH})_2$ -montmorillonite complex (which resembles the complex of Slaughter and Milne (1960) both for $d(\text{Å})$ values and intensities) is due to the excess $\text{Mg}(\text{OH})_2$ external to montmorillonite unit layers. Instead, Slaughter and Milne (1960) observed a high intensity third order peak for $\text{Mg}(\text{OH})_2$ -montmorillonite complex and explained

Table 1. X-ray diffraction data for $\text{Mg}(\text{OH})_2$ -montmorillonite complex, not washed with HCl

d(Å)	14.71	7.43	4.95	4.76	3.65	2.96	2.72	2.36	1.79	1.57
I	70	60	60	80	40	30	20	100	30	40

it due to the presence of poorly crystallized separate brucite phase giving a diffraction maximum in the vicinity of 4.9 Å.

No change in the X-ray pattern was observed for 10 days (Fig. 1). The relative intensities of the first and second order reflections as indicative of interlayering point to an interlayer population having sufficient brucite. The freshly prepared samples did not show any expansion of the 14.71 Å peak on glycerol treatment, but collapsed to 14.1 Å on heating (550°C, 2 hr). The free $\text{Mg}(\text{OH})_2$ present changed to MgO as shown by the X-ray analysis. Presence of free brucite can be a factor for the behaviour observed on heat and glycerol treatment. Non uniformity and/or incomplete chloritization are responsible for this behaviour but further attempt was not made to elucidate it. Grim and Johns (1954) on the other hand have reported a mineral with "islands" of brucite to keep the layers apart on heating but too few in number to prevent expansion with glycol. The hydroxy aluminum-montmorillonite complex prepared under similar

conditions did not exhibit this characteristic (Gupta and Malik, 1969).

After 10 days intensities of the brucite peaks started increasing (Fig. 2), with a corresponding decrease for the intensities of the peaks for the $\text{Mg}(\text{OH})_2$ -montmorillonite complex. Separate peaks for montmorillonite (along with brucite and the $\text{Mg}(\text{OH})_2$ -montmorillonite complex) were observed after 90 days. These results are in conformity with the data of Slaughter and Milne (1960), who observed a decrease in the completeness of the brucite interlayer, and increase in the intensity of a separate brucite phase, upon ageing of the product in the final solution. The low water content of the dried specimen makes this reaction slow and time dependant, and is similar to the "seeding" effects of free bayerite observed with hydroxy aluminum-montmorillonite complexes (Gupta and Malik, 1969; and Turner and Brydon, 1967). Peaks for $\text{Mg}(\text{OH})_2$ -montmorillonite complex were still present (although of lesser intensity) at the end of an investigated period of 6 months.

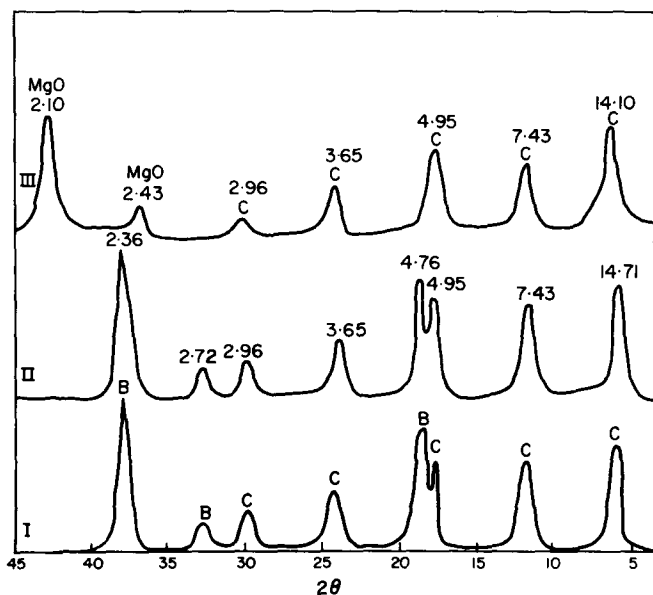


Fig. 1. X-ray diffraction patterns of $\text{Mg}(\text{OH})_2$ -montmorillonite complex not washed with HCl. Curve I, 10 days old sample; curve II, glycerol treated sample; curve III, sample heated. C, chlorite peaks; B, brucite peaks.

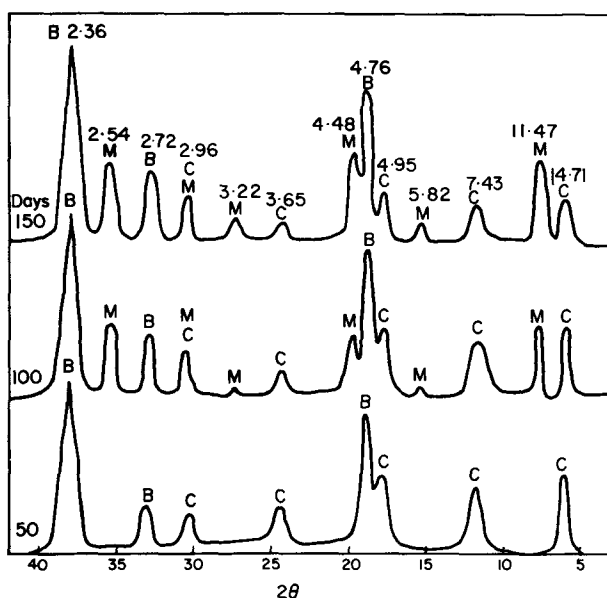


Fig. 2. X-ray diffraction patterns of $\text{Mg}(\text{OH})_2$ -montmorillonite complex not washed with HCl and the effect of time. C, chlorite peaks; B, brucite peaks; M, montmorillonite peaks.

$\text{Mg}(\text{OH})_2$ -montmorillonite complex (acid washed, system II). The $\text{Mg}(\text{OH})_2$ precipitated external to montmorillonite unit layers was removed immediately after precipitation, by dilute acid leaching. The quantity of the hydroxide thus leached out was 108 meq for 6 g montmorillonite. Exchangeable magnesium displaced by NaCl treatment was 0.15 meq per g complex, leaving approximately 16 meq $\text{Mg}(\text{OH})_2$ per g montmorillonite in a "fixed" form in its structure. This is the quantity (calculated) required for the transformation of montmorillonite to chlorite structure (Slaughter and Milne, 1960).

CEC values for montmorillonite and $\text{Mg}(\text{OH})_2$ -montmorillonite complex were 91 and 18 meq per 100 g clay. The values for the $\text{Mg}(\text{OH})_2$ -montmorillonite complex remained unchanged after another leaching with 0.5 N HCl.

The X-ray pattern of system II complex (Table 2) resembles that of the synthetic magnesium-chlorite (Slaughter and Milne, 1960). It did not show any change with time up to 3 months (Fig. 3). It confirms the view that only in the presence of free $\text{Mg}(\text{OH})_2$ (external to montmorillonite unit layers) will these complexes "expel" the "fixed" hydroxide interlayer. No peak for montmorillonite or the metal hydroxide was observed during this period. The well developed 14.71 Å basal spacing points towards the completeness of the brucite interlayer. On heating the sample, system II, (both

fresh and 3 months aged) to 550°C for 2 hr the X-ray pattern (Table 2) showed an increase in the intensity of the 001 reflection and a decrease in other reflections, without any change in basal spacing. The complex is unlike that of Slaughter and

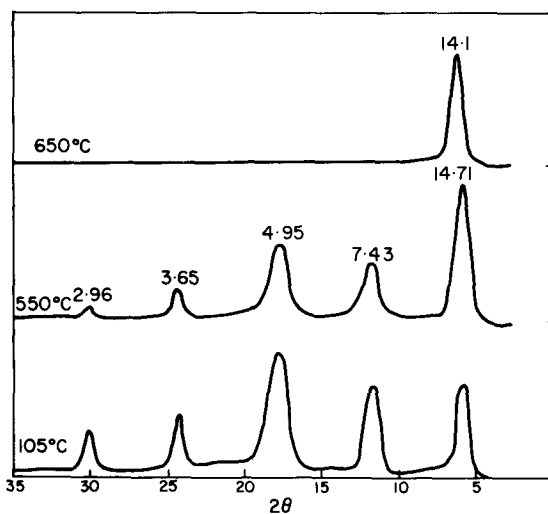


Fig. 3. X-ray diffraction patterns of acid washed $\text{Mg}(\text{OH})_2$ -montmorillonite complex (3 months aged) and the effect of heating.

Table 2. X-ray diffraction data of acid washed Mg(OH)₂-montmorillonite complex

d(Å)	14.71	7.43	4.95	3.65	2.96
I	100	70	90	40	30
I*	100	50	50	10	10

*Clay complex heated to 550°C.

Milne (1960) where only the 001 spacing is left. Only on heating to 650°C does the 001 reflection decrease to 14.1 Å. Such a collapse on heating is comparable to that reported for naturally occurring dioctahedral chlorites (Brydon *et al.*, 1961). At this temperature (650°C) the other order reflections disappear.

On none of these samples did the 001 spacing expand on glycerol treatment. The reaction resembles that of the complex of Slaughter and Milne (1960) who observed that fully developed interlayers give no evidence of expansion after ethylene glycol treatment. X-ray patterns of these samples after another acid leaching (0.5 N HCl) remained the same but after drastic treatment (2 N HCl in a boiling water bath for 2 hr) the residue gave broad peaks for montmorillonite.

Spacings of 14.71, 7.43, and 4.95 Å for the complex are higher than the normal 14.0–14.3, 7.1, and 4.7 Å of the 001, 002, 003 order reflections, respectively, for naturally occurring chlorites (McMurchy, 1934). Such spacings result from the need to accommodate the original exchange cations of the montmorillonite used for transformation (which in the new complex are not removed by 0.05 N HCl treatment).

Changes in the X-ray patterns of Mg(OH)₂-montmorillonite complex were observed after 3 months (Fig. 4). Peaks for brucite started appearing and increasing in intensity with time. This change was progressive but even at the end of 6 months ageing no peaks for montmorillonite were observed. On heating the 6 months aged sample to 550°C for 2 hr the 001 spacing collapsed to 14.4 Å with the remaining peaks for the complex disappearing. This aged sample on glycerol treatment showed a broad peak at 16.0 Å with the normal 001 reflection at 14.71 Å. The brucite peaks disappeared on leaching the sample with 0.05 N HCl and peaks for Mg(OH)₂-montmorillonite complex only were observed. CEC of this sample was found to be 21 meq per 100 g complex.

The X-ray data shows that under these conditions the synthesized chlorite-like structure remains stable only for 3 months. The appearance of peaks for brucite, collapse on heating at a lower temperature, expansion on glycerol treatment, and an increase in CEC of these aged samples points to some "backward" reaction resembling the "seeding" effects (Turner and Brydon, 1967). Although the expansion on glycerol treatment points to the presence of montmorillonite it seems that due to the slower rate of change ("backward" reaction) the quantity of the released montmorillonite is not sufficient to be traced by X-ray diffraction analysis. Rich (1968) has also indicated that the stability of Mg-OH interlayers in montmorillonite (formed only at a high pH of 10.0) decreased with time.

Thermal analysis. Differential thermal and thermogravimetric analysis of Mg(OH)₂-montmorillonite complexes (Gupta and Malik, 1968) lends

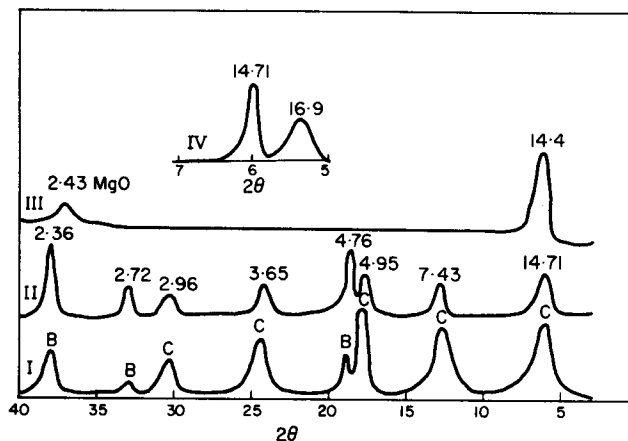


Fig. 4. X-ray diffraction patterns of acid washed Mg(OH)₂-montmorillonite complex. Curve I, 120 days aged sample; curve II, 150 days aged sample; curve III, 6 months aged sample heated to 550°C; curve IV, 6 months aged sample on glycerol treatment.

support to this X-ray and chemical data. Thermal analysis of the 6 months aged samples did not show any change or peaks for brucite or montmorillonite, which supports the assumption of an extremely slow rate of "backward" reaction on ageing.

Polarographic analysis. The polarographic reduction behaviour of these metal hydroxy-montmorillonite complex systems (Malik and Gupta, 1968b) both in the presence and absence of surface active agents also confirms the transformation of montmorillonite to new chlorite like structures.

I.R. analysis. The montmorillonite spectrum (Fig. 5) shows well pronounced absorption bands at 3703, 3450, 1655, and 1042 cm^{-1} (with some minor shoulders at 982 and 945 cm^{-1}). The major OH

towards the absence of any metal hydroxide external to montmorillonite layers. Somewhat different i.r. spectra from the one reported by Ahlrichs (1968) are primarily due to the different specimen of montmorillonite used for transformation.

Electrophoresis study. Migration of montmorillonite, magnesium hydroxy-montmorillonite complex particles (in a colloidal sol) towards the positive electrode indicates that both the montmorillonite and the synthesized complex are negatively charged. This suggests the formation of uncharged $\text{Mg}(\text{OH})_2$ interlayers.

A consideration of all these X-ray patterns, thermal analyses, polarographic reduction behaviour, i.r. spectra, CEC data, and electrophoretic studies stresses the conversion of montmorillonite to a

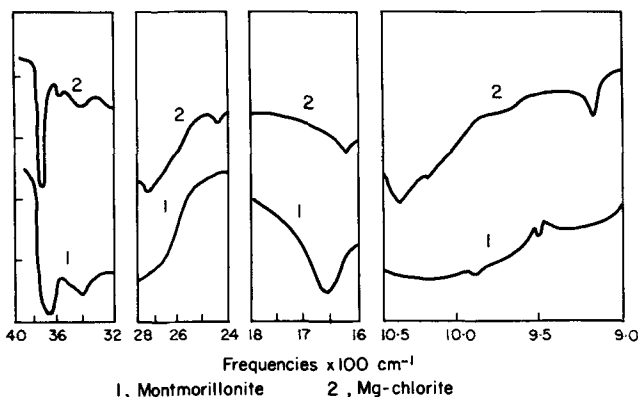


Fig. 5. I.R. spectrophotometric analysis.

absorption bands at 3703 and 3450 cm^{-1} resemble that of Bishui and Prasad (1960) for Otay California montmorillonite. The lattice OH band at 3700 cm^{-1} has been observed also for montmorillonite by Fripiat (1964). The Al-OH band, between 900–950 cm^{-1} , though not completely missing, is very broad.

Extra absorption bands appear in the $\text{Mg}(\text{OH})_2$ -montmorillonite complex (acid washed, system II) spectrogram at about 3780, 3600, 2750, 2445, and 910 cm^{-1} (with a shoulder band at 1315 cm^{-1}) pointing towards the development of new atomic groupings and possibly the transformation of the original montmorillonite structure. The band at 3703 cm^{-1} shown by montmorillonite seems to shift to 3780 cm^{-1} on chloritization. Ageing of the specimen did not change the spectra in any way. Synthesized brucite did not show any spectra.

The spectra for system II complex (both fresh and 6 months aged) after heating (200°C, 2 hr, Wiesmiller *et al.*, 1967, or after another acid leaching, 0.5 N HCl) did not change, pointing

magnesium-chlorite-like structure by the precipitation of $\text{Mg}(\text{OH})_2$ within the interlayer space of montmorillonite, under these conditions. Further, this conversion is stable only for a period of 3 months; after this period an extremely slow "backward" reaction starts taking place with the release of brucite and possibly montmorillonite also.

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Résumé—Un complexe de magnésium hydroxyde-montmorillonite préparé à un taux moléculaire de OH/Mg de 2 (16 meq Mg/g argile) et immédiatement nettoyé de tout Mg(OH)₂ libre se comporte comme du magnésium-chlorite et ne montre aucun changement au cours d'un vieillissement de 3 mois. L'hydroxyde de magnésium précipite complètement à l'intérieur de l'espace entre les couches de montmorillonite.

L'analyse de diffraction aux rayons X, les études thermiques (DTA et TGA), l'analyse d'absorption à l'infrarouge, le comportement de réduction polarographique et les mesures de capacité d'échange de cations confirment la transformation de la montmorillonite en une structure ressemblant au chlorite.

Un vieillissement supplémentaire du complexe résulte en un dégagement de brucite de l'espace entre les couches et l'expansion du complexe sur le traitement du glycérol. L'analyse aux rayons C d'échantillons vieux de 6 mois montre la présence de brucite libre mais aucune montmorillonite. Une hausse faible mais significative dans le CEC du complexe est observée pendant le vieillissement.

Quand le complexe Mg(OH)₂-montmorillonite est autorisé à vieillir en présence de Mg(OH)₂ libre, on observe un effet de "nucléation" et le Mg(OH)₂ "fixé" commence à sortir de l'espace entre les couches après une période de 10 jours.

Kurzreferat—Ein Magnesiumhydroxyd-Montmorillonite Komplex, der bei einem OH/Mg Molarverhältnis von 2 (16 mÄq Mg/g Ton) bereitet und sofort von etwa vorhandenem, freiem Mg(OH)₂ befreit worden ist, verhält sich wie Magnesium-Chlorit und zeigt während einer Alterung von 3 Monaten keine Veränderung. Magnesiumhydroxyd präzipitiert vollkommen innerhalb des Zwischenschichttraums des Montmorillonits.

Die Röntgenbeugungsanalyse, thermische (DTA und TGA) Untersuchungen, Ultrarota absorptionsanalyse, Messungen des polarographischen Reduktionsverhaltens und der Kationenaustauschkapazität bestätigen die Umwandlung der Montmorillonitstruktur in eine chloritartige Struktur.

Bei weiterer Alterung des Komplexes wird im Zwischenschichtenraum Brucit freigegeben und durch Behandlung mit Glycerin bläht sich der Komplex auf. Die Röntgenanalyse der 6 Monate alten Proben zeigt die Anwesenheit von Brucit, nicht aber von Montmorillonit an. Eine kleine aber bezeichnende Erhöhung im CEC des Komplexes wird bei der Alterung beobachtet.

Wird der Mg(OH)₂-Montmorillonit Komplex in der Gegenwart von freiem Mg(OH)₂ (außerhalb der Montmorillonitschichten) in trockenem Zustand der Alterung überlassen, so findet eine "Impfungswirkung" statt und das "gebundene" Mg(OH)₂ beginnt nach 10 Tagen aus dem Zwischenschichtraum herauszukommen.

Резюме—Комплекс монтмориллонита и гидроокиси магния, приготовленный при молярном отношении OH/Mg равном 2 (16 мэкв Mg/г глины) и немедленно очищенный от примеси свободной Mg(OH)₂, ведет себя как магниевый хлорит и не обнаруживает никаких изменений

свойств при старении в течение 3-х месяцев. Гидроокись магния, очевидно, полностью внедряется в межслоевые промежутки монтмориллонита.

Данные рентгеновского, термического (ДТА и ТГА) и инфракрасного анализа, а также изучение полярографических свойств и ионно-обменной емкости подтвердили превращение монтмориллонита в хлоритоподобную структуру.

При дальнейшем старении комплекса происходит выход брусита из межслоевых промежутков, в результате чего комплекс обретает возможность разбухать при обработке глицерином. Рентгеновский анализ образца после 6-ти месяцев старения установил присутствие свободного брусита, но не монтмориллонита. В процессе старения наблюдается не очень большое, но заметное увеличение ионно-обменной емкости.

При старении комплекса $Mg(OH)_2$ -монтмориллонит в присутствии свободной гидроокиси магния $Mg(OH)_2$ (находящейся вне монтмориллонитовых слоев) в сухом состоянии выход «зафиксированной» $Mg(OH)_2$ из межслоевых промежутков монтмориллонита начинается через 10 дней.