TRANSFORMATION OF MONTMORILLONITE TO NICKEL-CHLORITE

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Abstract—Nickel-chlorite has been obtained by the co-precipitation of nickelous hydrous oxide and montmorillonite at an OH/Ni ratio of 2.0. Chemical analysis shows that 16 me of Ni is fixed per gram of clay. System without any free nickelous hydrous oxide is quite stable up to an investigated period of 6 months, shows impedance to collapse on heating to 550°C, and no expansion of 001 spacing on glycerol treatment.

Different properties studied (X-ray diffraction analysis, thermal [D.T.A. and T.G.A.] data, i.r. absorption analysis, polarographic reduction behavior and cation exchange capacity measurements) confirm the complete transformation of montmorillonite to nickel-chlorite.

"Seeding" of the hydroxide out of the "fixed" interlayer positions takes place on ageing the sample with free nickelous hydrous oxide. No montmorillonite could be detected by X-ray diffraction analysis in spite of this backward reaction.

INTRODUCTION

Information on nickel-bearing clays is fragmentary. Spangenberg (1938) has described some nickel-bearing silicates including pimelite (nickel-montmorillonite) and schuahardite (nickel-chlorite). X-ray powder data on synthetic nickel-serpentine are reported by Feitknecht and Berger (1942) and Roy and Roy (1954).

Very few attempts have been made on the transformation of montmorillonite to nickel-chlorite. Slaughter and Milne (1960) were the first to give some X-ray diffraction data of nickel-chlorite obtained by co-precipitating nickel hydroxide and montmorillonite. Studies on i.r. absorption analysis have been undertaken by Ahlrichs (1968) of nickel hydroxide-montmorillonite interlayers.

The technique of preparing hydroxy-aluminum montmorillonite interlayers, reported in great detail and variation (Barnishel and Rich, 1965; Brydon and Kodama, 1966; Shen and Rich, 1962; Slaughter and Milne, 1960; Turner and Brydon, 1967; de Villiers and Jackson, 1967; and Hsu, 1968) has been utilized for the preparation of hydroxy-nickel montmorillonite interlayers. Properties (X-ray diffraction analysis, i.r. absorption analysis, and cation exchange capacity measurements) of hydroxy-nickel montmorillonite interlayers (shown to behave like nickel-chlorite, Gupta and Malik, 1968; Gupta and Malik, 1968) are discussed in this communication.

EXPERIMENTAL

Montmorillonite. The 2–0.2µ fraction of montmorillonite (supplied by B.D.H.) was obtained from water dispersed systems. No other preliminary treatment (or cation saturation) was given; in a similar study Slaughter and Milne (1960) and Barnishel and Rich (1965) have stressed the absence of any effects of homo-ionic saturation. The clay contained no organic matter. A 6 g portion of the clay was suspended in 100 ml of distilled water.

Precipitation of nickel-hydrous oxide. Nickel chloride (Analytical Grade) was added to the clay suspension to give a 2 N solution. This was neutralized by a controlled dropwise addition of 200 ml of normal NaOH solution at the rate of 1 ml per 5 min while mixing continuously at a high speed with a magnetic stirrer (approximately 2000 rmp) thus precipitating about 200 meq of nickel hydroxide per 6 g montmorillonite at a OH/Ni molar ratio 2-0, in about 17 hr. Triplicate experiments were conducted to check reproducibility of results. Blank experiments without adding the clay to a solution of nickel chloride, were also performed under similar conditions.

Nickel-hydroxide-clay complex (system no. I). The whole mass was then filtered, washed with a 1:1 ethanol-water mixture till free from chloride ions and dried at 105°C. No other cations except Na⁺ ions could be detected in the filtrate.

Acid washed nickel-hydroxide-clay complex (system no. II). In the second set of experiments after the precipitation the complex was mixed with 0-05 N HCl (preliminary experiments to estimate its quantity for dissolving only the free nickel-

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hydroxide, external to montmorillonite, were first conducted, stirred for 10 min and filtered. A stage was soon reached when increasing acid treatment did not leach more Ni\(^{2+}\) ions. After washing thoroughly, the residue was dried at 105°C.

**pH-measurement.** The pH at various stages was measured with a Cambridge Bench type pH-meter using glass calomel electrode assembly.

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

**Exchangeable nickel.** Ni was determined by displacing it from a 2-0 g sample of hydroxy-nickel-clay complex with 4 washes, each consisting of 25 ml of normal NaCl. No “fixed” nickel could be removed after NaCl treatment even with 0-5 N HCl. Nickel was estimated, wherever required, by EDTA titrations, dimethylglyoxime test as well as by polarographic reduction (Kolthoff and Lingane, 1952).

**X-ray diffraction.** Patterns were obtained on powder specimen (minus 300 British Standard Sieve) with Philips 1051 PW Diffractometer, using an iron target with manganese filter, at 26 kV and 10 mA. Different combinations of the beam, Soller and detector slits at a scan speed of 0-2° 2θ/min were used to provide greater precision in determining the 2θ values.

**I.R. analysis.** I.R. spectra were taken on a Perkin Elmer Spectrophotometer No. 021 with “nujol” mull specimen.

**Charge determination.** Migration of hydroxy-nickel-clay complex colloidal particles under the influence of an applied E.M.F. was seen in an electrophoresis apparatus (Burton Type). The boundaries of the colloidal suspensions always moved towards the positive electrode.

**RESULTS AND DISCUSSION**

**Montmorillonite.** X-ray diffraction data of montmorillonite (Table 1) used is comparable to that reported in Card No. 3-0019 (ASTM, STP, 48-L, X-ray Data File, 1962). On treatment with glycerol, the 001 spacing expands to 17-7Å, and on heating (600°C, 2 hr) it collapses to 9-3Å.

**Nickel chloride + sodium hydroxide system.** After precipitation, the pH of the mixture was 8-8. Nickel ions could not be detected in the filtrate. The dry precipitate contained 63-3% nickel corresponding to the composition Ni(OH)\(_2\). The X-ray diffraction pattern resembles that of \(\beta\) Ni(OH)\(_2\) of ASTM Card No. 1-1047. After heating to 600°C for 2 hr it changed to bunsenite, (NiO).

**Nickelous hydroxide oxide-clay complex (acid unwashed, system no. 1).** The pH of the montmorillonite suspension was 5-1 and after Ni(OH)\(_2\) precipitation it rose to 8-2. No cations except Na\(^+\) ions were present in the filtrate after precipitation of nickel. No chloride ions were adsorbed by the precipitated complex. Immediately after precipitation the product was amorphous to X-ray diffraction. After six hours, a complete pattern showing the presence of both nickel-chlorite and free nickel hydroxide oxide was observed. There was no peak for montmorillonite.

Peaks for nickel-chlorite are comparable with the data of Slaughter and Milne (1960). However, the 001 reflection, although of lower intensity, is not completely absent as was observed by them. It is rather doubtful whether the Ni(OH)\(_2\) (interlayer or free) will suppress these reflections. A shorter period of ageing can result in the absence of lower (d Å) spacings. After 15 hr the intensities for the nickel hydroxide oxide peaks started increasing with time with a corresponding decrease for the nickel-chlorite peaks (Fig. 1). It can be compared with the “seeding effect” of free aluminum hydroxide on bentonite precipitated with aluminum hydroxide (Turner and Brydon, 1967). Ageing of these products (in solution) results in a decrease in the completeness of the brucite-type layer of artificial structures (Slaughter and Milne, 1960). These data, in the solid state, show the importance of the presence of free metal hydroxide oxide. This change was continuous with time and was studied up to 6 months. Even at this stage, peaks for montmorillonite were absent.

No expansion of the 14-6Å line was observed on glycerol treatment at any time (Fig. 1).

**Nickelous hydroxide oxide-clay complex (pre-washed with 0-05 N HCl, system no. II).** Acid washing leached out 102 meq (for 6 g montmorillonite) of nickelous hydroxide oxide precipitated external to the montmorillonite unit layers. Exchangeable nickel displaced by NaCl treatment amounted to 0-2 meq per g clay. The rest of the hydroxide oxide (approximately 16-1 meq per g clay) was in a “fixed” form in the interlayer space of montmorillonite. Slaughter and Milne (1960) calculated the quantities of metal hydroxide oxides required for conversion of montmorillonite to chlorite structure and have shown it to be 16-0 meq per g clay.

CEC values for montmorillonite and nickelous hydroxide clay complex were 91-0 and 12-0 meq per 100 g clay respectively. The value for nickelous hydroxide oxide-clay complex did not change with 6 months ageing or after another acid leaching (0-5 N HCl).

The X-ray pattern of the System II (Table 4)
Fig. 1. X-ray diffraction traces (smoothed) of nickel hydroxy-clay complex (system 1) at different time intervals.

Table 1. X-ray diffraction data for montmorillonite

<table>
<thead>
<tr>
<th>d(Å)</th>
<th>11.47</th>
<th>5.82</th>
<th>4.48</th>
<th>3.22</th>
<th>2.92</th>
<th>2.54</th>
<th>2.48</th>
<th>2.33</th>
<th>1.69</th>
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<td>15</td>
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<td>70</td>
<td>35</td>
<td>20</td>
<td>40</td>
<td>65</td>
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Table 2(a). X-ray diffraction data for nickel hydroxide

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<th>d(Å)</th>
<th>4.61</th>
<th>2.70</th>
<th>2.33</th>
<th>1.75</th>
<th>1.56</th>
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<td>1</td>
<td>65B</td>
<td>100</td>
<td>60B</td>
<td>10</td>
<td>60</td>
<td>40</td>
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(b). X-ray diffraction data for bunsenite

<table>
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<th>d(Å)</th>
<th>2.41</th>
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<tr>
<td>1</td>
<td>90</td>
<td>100B</td>
<td>40</td>
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B - Broad peak

Table 3. X-ray diffraction for nickel hydrous oxide-clay complex

<table>
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<th>d(Å)</th>
<th>14.6</th>
<th>7.32</th>
<th>5.00</th>
<th>4.61</th>
<th>3.60</th>
<th>2.70</th>
<th>2.33</th>
<th>1.75</th>
<th>1.56</th>
<th>1.48</th>
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<td>45</td>
<td>85</td>
<td>55</td>
<td>45B</td>
<td>25</td>
<td>100</td>
<td>10B</td>
<td>10B</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>

resembles somewhat that of the nickel-chlorite of Slaughter and Milne (1960). It does not show any change with time (Fig. 2) up to the investigated period of 6 months, suggesting the high stability of the complex when free of external nickelous hydrous oxide. Presence of the well defined 001 (14.6 Å) peak differentiates this complex from the natural or synthetic nickel-serpentines studied.
Table 4. X-ray diffraction data for nickel-chlorite (acid washed)

<table>
<thead>
<tr>
<th>d(Å)</th>
<th>14-6</th>
<th>7-32</th>
<th>5-0</th>
<th>3-6</th>
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<tr>
<td>1</td>
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<td>30</td>
<td>15</td>
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<tr>
<td>1*</td>
<td>100</td>
<td>30</td>
<td>15</td>
<td>–</td>
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*Clay heated to 550°C.

No expansion of the 001 spacing on glycerol treatment was found, possibly because of the fully developed metal hydrous oxide interlayers. No change in the X-ray pattern was observed after leaching the sample with 0.5 N HCl. After drastic acid treatment (2 N HCl, in a boiling water bath, for two hr) the residue showed an amorphous character.

Fig. 2. X-ray diffraction traces (smoothed) of acid washed nickel-hydroxy clay complex (system II) at different time intervals.

by Feitknecht and Berger (1942) and Roy and Roy (1954).

On heating (550°C, 2 hr) System II it gives an X-ray pattern (Table 4) where the intensity of the 001 peak (14-6 Å) increases and that of the other reflections decreases without any change in basal spacings. The weak 004 reflection at 3-6Å disappear on heating. On heating to 650°C the 001 reflection collapses to 14-3 Å (as the interlayer hydrous oxide is dehydrated) and the other reflections disappear completely. This collapse on heating can be compared to that reported for naturally occurring dioctahedral chlorites (Brydon et al., 1961). Even after 6 months ageing of the sample, the 001 peak did not collapse below 14-3 Å on heating to 650°C.

Higher spacings of 14-6, 7-32 and 5-0 Å as compared to the normal 14-0–14-3, 7-1 and 4-7 Å of 001, 002, and 003 order reflections, respectively, of naturally occurring chlorites (McMurchy, 1934) result from the necessity of accommodating the original exchange cations of montmorillonite used for transformation and are in conformity with the observations of Slaughter and Milne (1960).

The chlorite structure so obtained is quite stable even when 16 meq of Ni(OH)₂ is precipitated per gram of montmorillonite and this result with nickelous hydrous-oxide-montmorillonite complex can be well compared with the aluminum hydrous oxide-montmorillonite complex (Gupta and Malik, 1968).

Thermal analysis. Differential thermal analysis
and thermo-gravimetric analysis of the metal hydrous oxide clay complexes support the chemical and X-ray analysis data (Gupta and Malik, 1968).

Polarographic analysis. The polarographic reduction behavior of these hydroxy-metal-montmorillonite complex systems, with and without the addition of surface active agents, also confirms the transformation of montmorillonite to a new structure (Malik and Gupta, 1968).

I.R. analysis. The montmorillonite spectrum (Fig. 3) shows well pronounced absorption bands at 3703, 3450, 1655 and 1042 cm\(^{-1}\) (with some minor shoulders at 982 and 945 cm\(^{-1}\)). The spectrum obtained as regards the major OH bands at 3703 and 3450 cm\(^{-1}\) resembles that of Bishui and Prasad (1960) for Otay, California montmorillonite. A lattice OH band at 3703 cm\(^{-1}\) has also been observed 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 nickelous hydrous oxide-clay complex (prewashed with 0.05 N HCl, System II) spectrogram at about 2750, 2445 and 910 cm\(^{-1}\) (with a shoulder band at 1310 cm\(^{-1}\)) pointing towards the development of new atomic groupings and possibly the transformation of the original montmorillonite structure. Nickel hydrous oxide did not show any bands other than the OH or H\(_2\)O bending vibrations. Spectra remained unchanged on ageing these samples for 6 months. Spectra obtained (System II) after heating (200°C, 2 hr, Weismliller et al., 1967) or another acid leaching (0.5 N HCl) did not change, confirming the absence of any metal hydrous oxide external to montmorillonite layers.

The spectra differ from that shown by Ahlrichs (1968) for his nickel-chlorite specimen due to the difference in the montmorillonite used for transformation and the methods (pH and quantity of nickel hydrous oxide interlayer) of transformation.

Electrophoresis study. Migration of both montmorillonite and nickelous hydrous oxide-clay complex particles (in a colloidal sol) towards the positive electrode indicates that these are negatively charged, suggesting the formation of uncharged hydroxy-metal interlayers in between the montmorillonite sheets rather than the adsorption of anionic clay on positively charged Ni(OH)\(_2\) polymers as postulated by Hsu and Bates (1964) for hydroxy-aluminum-montmorillonite complexes.

A consideration of all these X-ray patterns, thermal analysis, polarographic analysis, i.r. spectra, c.e.c. data and electrophoretic studies stresses the conversion of montmorillonite to nickel-chlorite by the precipitation of nickel-hydrous oxide within the interlayer space of montmorillonite.

Acknowledgments—Thanks are due to the Director and Dr. B. Rama Rao of the Regional Research Laboratory, Hyderabad (India) for their help in X-ray analysis and to the Director, Defence Science Laboratory, Delhi (India) for the help in i.r. analysis.

REFERENCES

Résumé – On a obtenu du chlorite de nickel en précipitant ensemble de l’oxyde de nickel hydraté et du montmorillonite à un rapport de OH/Ni de 2.0. L’analyse chimique montre que pour un gramme d’argile, il y a 16 meq de Ni. Sans oxyde de nickel hydraté libre, le système est assez stable pendant une période étudiée de six mois; il montre une certain résistance à la désintégration quant on chauffe à une température de 550°C, et aucune extension de l’écartement 001 par le traitement au glycérol.

Les différentes propriétés étudiées (analyse de diffraction des rayons X, données thermiques (D.T.A. et T.G.A.), analyses d’absorption d’infra-rouge, comportement de la réduction polarographique et mesures de capacité d’échange de cations) confirment la transformation complète du montmorillonite en chlorite de nickel.

La "semence" de l’hydroxyde à partir de positions "fixes" dans les couches intermédiaires se produit avec le vieillissement du prélèvement, l’oxyde de nickel hydraté étant libre. En dépit de cette réaction inverse il a été possible de détecter du montmorillonite par l’analyse de diffraction des rayons X.


"Impfung" des Hydroxyds von den "festen" Zwischenschichtpositionen aus erfolgt beim Altern der Probe mit freiem Nickelhydroxydul. Trotz dieser rückläufigen Reaktion konnte kein Montmorillonit durch Röntgenbeugungsanalyse festgestellt werden.

Резюме—Никелевый хлорит был получен путем соосаждения гидроокиси никеля и монтмориллонита при отношении OH:Ni= 2:1. По данным химического анализа, 1 г. глины поглощает 16 мг анионов никеля. Полученный продукт, не содержащий свободной гидроокиси никеля, является совершенно стабильным в течение 6 месяцев (длительность исследования), обнаруживает признаки начинающегося распада при нагревании до 550°C, при его обработке глицерином значение расстояния 001 не увеличивается.
Результаты рентгеновского изучения, термического анализа (ДТА, ТГА), инфракрасной спектроскопии, полярографической редукции (определение обменного никеля) и изучения способности к обмену катионов подтверждают полное превращение монтмориллонита в никелевый хлорит.

При старении осадка, содержащего свободную гидроокись никеля, последняя обособляется и оказывается не связанной с определенными межслоевыми позициями; несмотря на этот обратный процесс, в том же веществе монтмориллонит рентгеновским методом не обнаружен.