REHYDRATION OF CALCINED Mg-Al HYDROTALCITE IN ACIDIFIED CHLORIDE-CONTAINING AQUEOUS SOLUTION

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The rehydration of periclase-like Mg-Al mixed oxide obtained by calcination of hydrotalcite-like precursor with a Mg/Al molar ratio of 2 was carried out in KCl–HCl solutions at various pH and constant concentration of Cl^-. A buffer equilibrium accompanied by leaching out of Mg^{2+} cations from the solid was observed during rehydration, when reconstruction of the layered hydrotalcite structure takes place. With increasing HCl concentration in the rehydration solution, the Mg/Al molar ratio in the obtained solid gradually decreased from about 1.5 to 0.3. An anomaly was found, when the increasing concentration of acid resulted in increasing pH of final solution. The XRD measurements showed that the initially formed hydroxide form of hydrotalcite is transformed into randomly interstratified forms of the Mg-Al hydroxide hydrate/Mg-Al chloride hydroxide hydrate, which are accompanied by the release of OH^- anions into solution. The crystalline structure of rehydrated product decreased as Mg^{2+} cations were released into solution, which was accompanied by incorporation of Cl^- into the solid.

Keywords: Hydrotalcite; Layered double hydroxide; Magnesium; Aluminum; X-ray powder diffraction; Rehydration-reconstruction process.

Hydrotalcite, a magnesium aluminum carbonate hydroxide, is a naturally occurring mineral of chemical composition $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. This mineral exhibits a layered crystal structure, which is similar to that of brucite, $Mg(OH)_2$, where each Mg^{2+} cation is octahedrally surrounded by six OH^- anions and the different octahedra $[Mg(OH)_6]^{4-}$ share edges formig infinite sheets. The sheets are stacked one on the top of an other being held together by weak interactions via hydrogen bonds. In the hydrotalcite, the Mg^{2+}/Al^{3+} isomorphous substitution in octahedral sites of the hydroxide sheet results in a net positive charge, which is neutralized by the interlayer anionic species. Hydrotalcite has been taken as a reference name for many

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isomorphous compounds with various chemical composition, which can be represented by the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n-valent anion and x has usually values between 0.20 and 0.35.

Hydrotalcite-like compounds find a great variety of uses in many applications, e.g. in heterogeneous catalysis, polymer processing, pharmacy, adsorption and decontamination processes[1–4]. These materials are characteristic by a weak bonding between the interlayer anions and the host structure; hence, anion-exchange reactions can proceed under suitable conditions. Carbonate is the most preferred anion in these reactions and the replacement of interlayer CO_3^{2-} anions by anion exchange is almost impossible. Therefore, the synthesis of hydrotalcite-like compounds with other anions than carbonate requires the performance of the reaction under carbonate- and CO_2-free conditions, when common preparation techniques such as coprecipitation are employed.

An alternative procedure used for incorporation of other anions into the hydrotalcite structure is the rehydration of a thermally decomposed hydrotalcite-like precursor in a solution containing the desired anionic species. During hydrotalcite heating, the interlayer water is first released at first and then the loss of OH^- of hydroxide layers accompanied by loss of interlayer anions occurs. The layered crystal structure of hydrotalcite collapses to form periclase-type Mg-Al mixed oxide. At high calcination temperatures above 900 °C, the crystallization of $MgAl_2O_4$ spinel together with periclase (MgO) is observed[5]. Mixed oxides prepared at moderate calcination temperatures of about 400–600 °C can rehydrate in aqueous media. During the rehydration, a reconstruction of the layered hydrotalcite structure with incorporation of anions from solution takes place. The rehydration-reconstruction procedure is often used for preparation of hydrotalcite-like compounds intercalated with various anions. It can be also applied in water decontamination when the calcined hydrotalcite is used as a sorbent for removal of undesirable anionic species. Applications of hydrotalcite-like compounds in water decontamination are discussed in detail in ref.[2]. After regeneration in a carbonate-containing solution and subsequent thermal treatment, the sorbent can be reused in the decontamination[6].

The utilization of hydrotalcite-related Mg-Al mixed oxides with various Mg/Al ratios for removal of chlorides from aqueous solution was recently studied. The rehydration was carried out in the presence of hydrochloric acid[7,8], with rehydration-reconstruction and neutralization processes occuring simultaneously. Chloride removal in the presence of various cations, e.g. Na^+, Mg^{2+}, Al^{3+}, Ca^{2+} or NH_4^+, has been also examined[9–11].

In the present study, the rehydration of Mg-Al mixed oxide in dilute hydrochloric acid is examined in dependence on the solution pH, when the calcined hydrotalcite with Mg/Al molar ratio of 2 is added to HCl–KCl aqueous solution at constant ionic strength. During rehydration reaction, a simultaneous incorporation of Cl^- and OH^- anions into hydrotalcite interlayers takes place. In anion-exchange reactions, the OH^- anions are more preferred in comparison with Cl^- [12,13], which can impede the chloride incorporation into the rehydrated product. The chloride removal in the presence of other cations was already reported but a detailed study dealing with the effect of the concentration of accompanying cations is missing. The obtained results could contribute to explanation of the rehydration mechanism of hydrotalcite-related mixed oxides.

EXPERIMENTAL

Preparation of Calcined Hydrotalcite

The hydrotalcite-like precursor was prepared by coprecipitation. An aqueous solution (450 ml) of $Mg(NO_3)_2\cdot6H_2O$ and $Al(NO_3)_3\cdot9H_2O$ with a Mg/Al molar ratio of 2 and total metal ion concentration of 1.0 mol l^{-1} was added dropwise to 200 ml of 0.5 M Na_2CO_3 solution under vigorous stirring. The temperature was maintained at 75 °C and pH at 10.0 ± 0.1 by a simultaneous addition of 3 M NaOH. The addition of both solutions took 1 h. The resulting suspension was then maintained at 75 °C with stirring for 1 h. The product was filtered off, washed several times with distilled water and dried at 105 °C overnight. The dried product (size the particles max. 10–11 μm) was heated at 450 °C for 3 h (heating rate 15 °C min^{-1}) and then cooled to room temperature in a desiccator. The calcined product was immediately used for rehydration experiments.

Rehydration

The rehydration of calcined hydrotalcite (CHT) was carried out in batch arrangement at room temperature. A series of 13 samples consisting of 50 ml of rehydration solution of various pH was prepared as follows. The HCl solution (c = 1.0 mol l^{-1}) ranging from 0 to 40 ml was diluted with 10 ml of distilled water; the constant ionic strength of the solution was provided by addition of a corresponding volume of 1 M KCl (40–0 ml). In this way 50 ml of rehydration solution was obtained. The rehydration solutions were placed in 100-ml PE bottles, each containing 1 g of calcined hydrotalcite, and the bottles were sealed. After short intensive mixing, the suspensions were kept at rest at room temperature for 150 h.

Then the suspensions were filtered and pH of the filtrates was measured. The obtained values were employed for plotting a dependence of solution pH on acid concentration, the acid neutralizing capacity (ANC) curve. Concentrations of Mg and Al in filtrates were also determined. Rehydrated solid samples (RHT) were dried without any washing at room temperature. The rehydration procedure and all measurements were repeated three times and the obtained results were averaged. A list of prepared samples is presented in Table I. The label of each sample corresponds to the amount of HCl in solution (e.g., in preparation of RHT 9, 9 ml of 1 M HCl in 50 ml solution was used).

Sample Characterization

Chemical analysis of solid samples was carried out after their dissolution in dilute HNO_3 (1:4). Mg, Al and Cl contents in solution were determined by chelatometric and argentometric titration, the K content was determined by AAS using a Varian SpectrAA–30/40 spectrometer (acetylene-air flame).

The X-ray powder diffraction patterns of rehydrated samples were recorded with Ge-monochromatized $CuK\alpha_1$ radiation in the reflection mode, on an INEL CPS 120 diffractometer equipped with a 120° curved position-sensitive detector. All patterns were recorded at 30 kV and 20 mA and exposure time 2000 s, with the samples in a flat rotation holder. Each sample was measured three times and resulting *d* are average values.

Solid-state NMR spectroscopy was employed to obtain ^{27}Al MAS NMR spectra. They were measured at 11.7 T using a Bruker Avance 500 WB/US NMR spectrometer equipped with a double-resonance 4-mm probehead. The ^{27}Al MAS NMR spectra were acquired at 130.287 MHz, spinning frequency $\omega_r/2\pi$ = 10 kHz, 20° pulse width 1 μs and recycle delay 1 s. The spectra were referenced to $Al(NO_3)_3$ (0.0 ppm).

RESULTS AND DISCUSSION

The calcined hydrotalcite (CHT) was rehydrated in aqueous solutions of various acidity, with the initial HCl concentration of 0–0.8 mol l^{-1}. The ionic strength of the solution was kept constant by addition of KCl solu-

TABLE I
Results of chemical analysis of rehydrated samples (RHT) after rehydration of calcined hydrotalcite in acidified aqueous solution (selected points of ANC curve)

Sample	c_{HCl}[a] mol l^{-1}	Mg	K	Al	Cl	CO_3^{2-}	Molar ratio	
		wt.%					Mg/Al	Al/(Mg + Al)
RHT 0[b]	0	8.91	6.92	5.03	9.63	–	1.97	0.336
RHT 9	0.18	11.08	5.04	7.99	14.10	1.60	1.54	0.394
RHT 12	0.24	8.26	7.50	7.45	15.47	0.81	1.23	0.448
RHT 15	0.30	8.89	5.38	8.53	15.30	0.76	1.16	0.463
RHT 18	0.36	7.92	4.44	10.68	18.05	0.41	0.82	0.548
RHT 20	0.40	6.17	3.44	11.98	10.83	0.22	0.57	0.636
RHT 30	0.60	3.55	0.99	12.19	–	0.21	0.32	0.756

[a] Initial HCl concentration in solution used for rehydration. [b] RHT 0 was obtained by rehydration of calcined hydrotalcite in aqueous KCl solution (0.8 mol l^{-1}) without HCl.

tion. The resulting ANC curve (Fig. 1) demonstrates the dependence of pH value measured in filtrate after rehydration reaction on the initial HCl concentration. The course of measured ANC curve is similar to that reported e.g. for alkaline soils[14,15] or metallurgical slags[16]. However, a marked difference was observed in the buffer part of the ANC curve, where the solution pH increased with increasing concentration of HCl. Therefore we have focused on the buffer interval (corresponding approximately to an initial HCl concentration of 0.18–0.60 mol l^{-1}) to explain this anomaly on the ANC curve. A partial dissolution of solid samples during rehydration in acidified solution can be expected and therefore the concentration of metal cations (Mg^{2+}, Al^{3+}, and K^+) in the filtrate obtained after the reaction was determined. The dependences of Mg^{2+} and Al^{3+} concentrations and solution pH on the initial concentration of HCl are presented in Fig. 2. The results of chemical analysis of rehydrated products are summarized in Table I. The CO_3^{2-} content of about 2 wt.% was determined in the RHT 0 sample. The carbonate content decreased with the addition of HCl from 1.6 wt.% in RHT 9 sample to 0.21 wt.% in RHT 30 sample (Table I).

In Fig. 2 it is evident that the mentioned buffer interval is related to the leaching of magnesium and aluminium cations from rehydrated samples into solution. Aluminium was leached just after termination of the magnesium buffer interval. The pH values decreased down to the buffer interval of aluminium (pH ~ 3.8), which was set up at initial HCl concentration higher

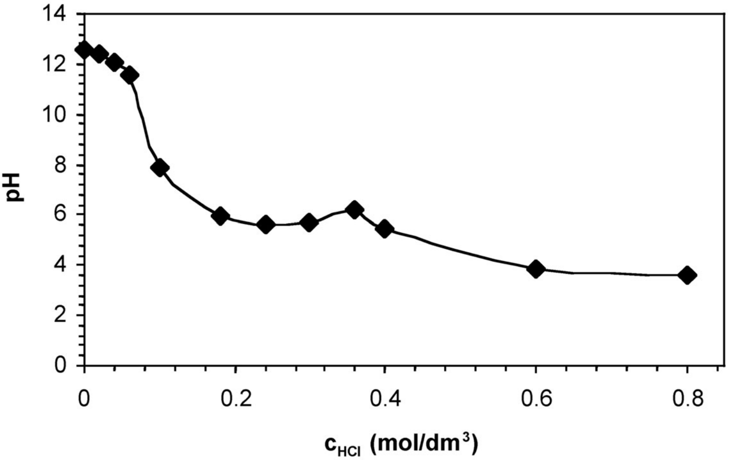

FIG. 1
ANC curve of calcined hydrotalcite in HCl–KCl aqueous solution

than 0.60 mol l^{-1} (Fig. 1). Selective leaching of Mg^{2+} and Al^{3+} cations can be explained by different stability of hydrated Mg and Al oxides in acid solutions. Stability of $Mg(OH)_2$ and $Al(OH)_3$ has been reported by Tamura et al.[17]. The solubility of $Mg(OH)_2$ increases linearly with decreasing solution pH; it dissolves in the region of $Al(OH)_3$ stability at pH interval ca. 9–4. The solubility of $Al(OH)_3$ exhibits a minimum at pH ca. 6; it dissolves in acid (pH < 4) or alkaline (pH > 11) solutions. Nevertheless, the selective dissolution of the hydroxides cannot explain the pH anomaly on the ANC curve.

In order to determine possible changes of Al^{3+} coordination in the solid, the ^{27}Al MAS NMR spectra of the rehydrated samples were measured. The Al cations both in tetrahedral (76 ppm) and octahedral (10 ppm) coordination were detected in calcined hydrotalcite but the spectra of rehydrated products showed Al cations only in octahedral coordination (Fig. 3). No significant changes in coordination of Al the studied RHT samples were found. Nevertheless, there is an increase in the band at ca. 5 ppm for RHT samples, which may be due to structural defects in solid phase. The local Al environment in sample RHT 9 may be less disordered than in RHT 30.

The maximum on the pH–c_{HCl} plot (Fig. 2) can be interpreted as follows. The increasing HCl concentration is neutralized with the $Mg(OH)_2$ leaching:

$$Mg(OH)_2(s, \text{hydrotalcite}) + 2\ H_3O^+(aq) \rightarrow Mg^{2+}(aq) + 4\ H_2O(l)\ .$$

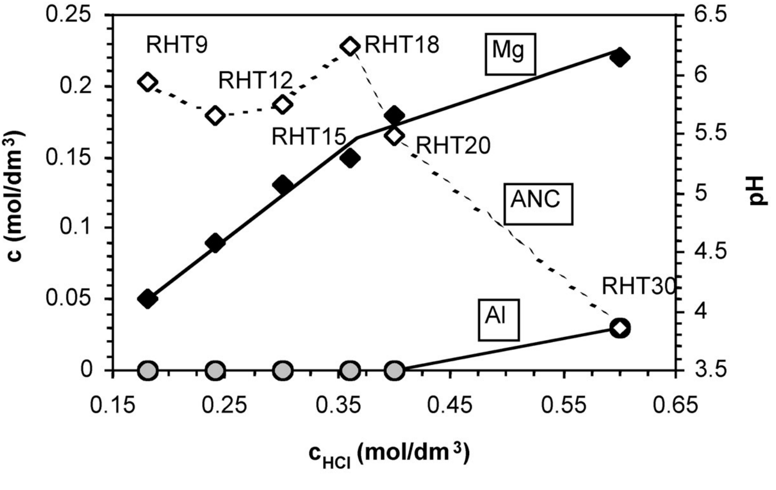

FIG. 2
Concentration of leached cations (Mg^{2+} and Al^{3+}) and pH of the final solution obtained after rehydration of calcined hydrotalcite in dependence on the initial HCl concentration

Together with Mg^{2+} leaching, an other effect can influence the final solution pH. During rehydration, the calcination product (Mg-Al mixed oxide) is rehydrated to restore the layered hydrotalcite structure, in which OH^- anions are incorporated as interlayer anions, i.e. the hydroxide form of rehydrated hydrotalcite is formed first. In solutions with higher HCl concentrations, the interlayer OH^- anions are exchanged for Cl^-. In the anion-exchange reactions, the OH^- is more preferred to Cl^- [18] and the hydroxide form of the rehydrated product is more stable than the chloride form. Therefore, the anion exchange of OH^- for Cl^- occurs mainly in the more acidified solutions, with higher concentration of hydrochloric acid. Content dependency of Cl^- ions in solid samples is presented in Fig. 4. It is evident, that maximum Cl^- content in the RHT 18 sample corresponds to OH^- maximum in the final solution. Simultaneous Mg^{2+} leaching and OH^- release may cause a pH increase in the solution obtained after rehydration reaction.

To support this findings, confrontation with the powder XRD analysis is performed. It is well known that the hydrotalcite-like compounds exhibit rhombohedral symmetry with three hydroxide layers per unit cell. The basal spacing d_{003} is an important structure parameter depending both on the size of interlayer anions and a net positive charge of the hydroxide

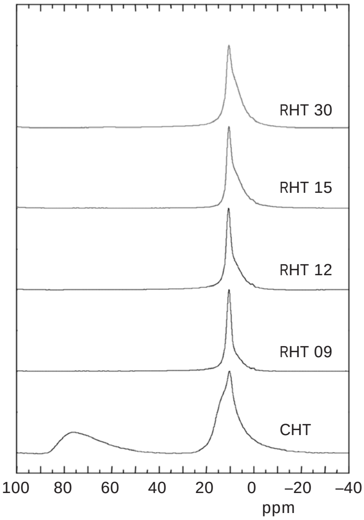

FIG. 3
The ^{27}Al MAS NMR spectra of calcined hydrotalcite (CHT) and samples rehydrated in HCl–KCl aqueous solution (RHT)

layers, which is given by the extent of M^{II}/M^{III} isomorphous substitution in octahedral sites of brucite-like sheet. The basal spacings 0.76 and 0.79 nm were reported for Al-rich and Al-poor hydrotalcite-like compounds, respectively[19,20]. The powder XRD patterns of rehydrated samples in Fig. 5 docu-

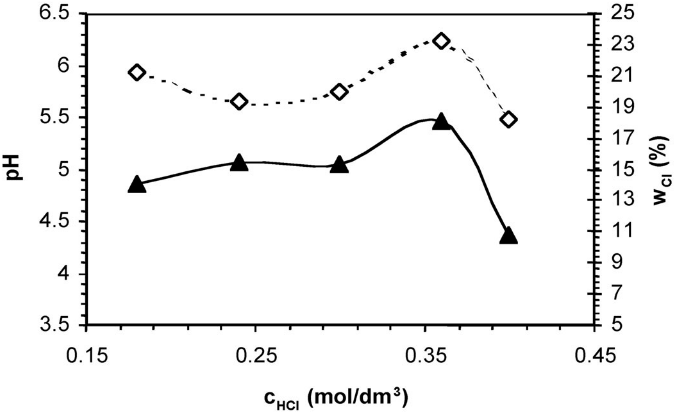

FIG. 4
Concentration of Cl⁻ anion and pH of the final solution obtained after rehydration of calcined hydrotalcite in dependence on the initial HCl concentration; ◇ pH, ▲ chloride

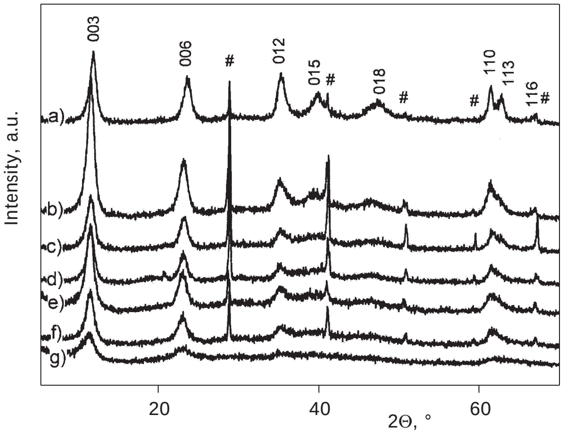

FIG. 5
Powder XRD patterns of samples after rehydration of calcined hydrotalcite in HCl-KCl aqueous solution (no washing used): a RHT 0, b RHT 9, c RHT 12, d RHT 15, e RHT 18, f RHT 20 and g RHT 30 (# = KCl)

ment reconstruction of the layered hydrotalcite structure in the rehydration of the calcined hydrotalcite-like precursor. The basal diffraction lines of rehydrated samples show a tendency to intensity decrease and broadening with increasing concentration of HCl in solution. The phases in powder XRD patterns identified using the ICDD-PDF database imply a transition between the hydroxide form of hydrotalcite (Mg-Al hydroxide hydrate, HH, $Mg_4Al_2(OH)_{12}(OH)_2 \cdot 3H_2O$, ICDD-PDF No. 35-964) and Mg-Al chloride hydroxide hydrate (HC, $Mg_xAl(OH)_{2x+2}Cl \cdot yH_2O$, ICDD-PDF No. 19-748). The basal spacing corresponding to one layer of the HH structure is d = 0.755 nm [19] and of the HC structure is d = 0.786 nm [20].

The rehydrated RHT 0 sample shows in the powder XRD pattern sharp and intense basal diffraction lines (003 and 006) and broad non-basal lines with lower intensity characteristic of hydrotalcite-like compounds (Fig. 5). RHT samples rehydrated in HCl–KCl solution contain additional peaks of KCl. The basal diffractions correspond to successive orders of the basal spacing, depending on the layer stacking sequence. When we recalculate basal d values for one layer from the 003 and 006 diffraction lines of the RHT samples and of the HH and HC, we obtain the relation in Fig. 6. This relation presents evidence that the RHT samples are interstratified layered materials. The divergence of values from HH is moderate for RHT 0 sample and in-

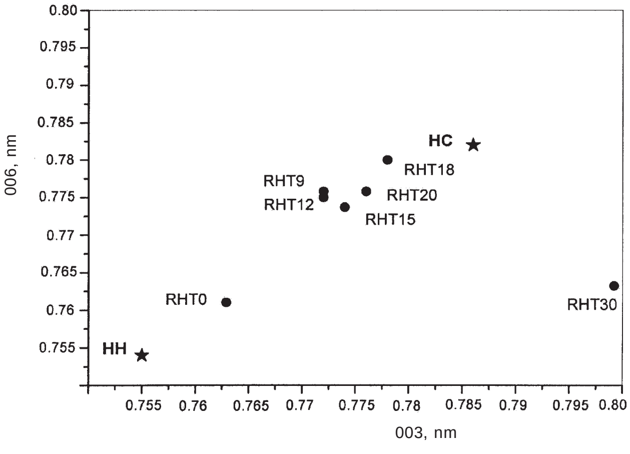

FIG. 6
Basal spacing (in nm) calculated for one layer from 003 and 006 diffraction lines. The data obtained for rehydrated samples (RHTs) are compared those published for HH [19], Mg-Al hydroxide hydrate, and HC [20], Mg-Al chloride hydroxide hydrate

creases with changing the HH/HC layer composition in RHT samples. The similar interstratification of the HH/HC phases appears in RHT 9, RHT 12, RHT 15 and RHT 20 samples when the RHT 18 sample is very close to the HC structure[20]. The RHT 30 sample exhibits in XRD pattern low-intensive and broad diffraction lines because of the strong acid solution used for rehydration, which prevents regeneration of the layered hydrotalcite structure.

CONCLUSIONS

The acid neutralizing capacity (ANC) measurement was used to study the rehydration of calcined hydrotalcite in HCl–KCl aqueous solutions. A significant Mg^{2+} buffer equilibrium on the ANC curve was found. The Mg/Al molar ratio in rehydrated solids decreased with increasing HCl concentration from 1.54 to 0.32. An anomaly on the ANC curve was found when the increasing acid concentration resulted in increasing pH of final solution. The NMR analysis revealed that the anomaly is not associated with coordination of Al cations. Together with Mg^{2+} leaching, an other process takes place, a transition of the primarily formed hydroxide form of rehydration product to the chloride, resulting in an increase in OH^- concentration in the final solution. The anion exchange occurs mainly in the solutions with higher HCl concentration because of a higher stability of hydroxide than chloride form of the rehydration product. Simultaneous leaching of Mg^{2+} and release of OH^- ions can cause an anomaly on the ANC curve, when final solution pH increases with increasing concentration of the acid.

The XRD analysis implies that rehydrated calcined Mg-Al hydrotalcites are interstratified structures formed by Mg-Al hydroxide hydrate and Mg-Al chloride hydroxide hydrate phases.

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SYMBOLS AND ABBREVIATIONS

ANC	acid neutralizing capacity
CHT	calcined hydrotalcite
RHT	rehydrated solid samples
HH	Mg-Al hydroxide hydrate ($Mg_4Al_2(OH)_{12}(OH)_2\cdot 3H_2O$)
HC	Mg-Al chloride hydroxide hydrate ($Mg_xAl(OH)_{2x+2}Cl\cdot yH_2O$)
d_{003}	basal spacing, nm

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