

# Synthesis and Characterization of Lamellar Cadmium Aluminum Hydroxide Salts with $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ , $\text{Cl}^-$ , and $\text{NO}_3^-$

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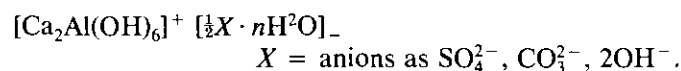
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This paper concerns the synthesis, structural characterization, and compositional changes ( $\text{H}_2\text{O}$ ) of layered Al/Cd oxide hydroxide salts with different interlayer anions. The chemical compositions can be given by:  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdX} \cdot n\text{H}_2\text{O}$ ,  $X = \text{SO}_4^{2-}$ ,  $2\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $2(\text{NO}_3^-)$ . The structural model was proven by calculated X-ray powder patterns, which were created similarly to the isostructural Ca–Al hydroxide salts. The structural composition can be given by a main layer and an interlayer:  $[\text{Cd}_2\text{Al}(\text{OH})_6]^+ [\frac{1}{2}X \cdot n\text{H}_2\text{O}]^-$ . The water content of the interlayer is dependent on temperature, relative humidity, and interlayer anions. The X-ray powder pattern, thermal, and IR spectroscopical data were determined. This paper is a contribution to the knowledge on systems, which have gained increased interest recently in terms of application to environmental problems. © 1994 Academic Press, Inc.

## 1. INTRODUCTION

Lamellar calcium aluminum hydroxide salts occur in the hydration process of cementitious materials. Recently these structure types were investigated for their ability for fixation of hazardous elements.

The composition can be given by a layer structure composed of a positive charged main layer and a negative charged interlayer:



The different water contents vary on relative humidity, interlayer anions, and temperature. The variation of the interlayer with different anions was described by (9, 11–13, 15). A variation of the main layer is reported on replacement of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ga}^{3+}$  (10). Concerning the replacement of  $\text{Ca}^{2+}$  by  $\text{Cd}^{2+}$  only less data are available (2).

The structural model of compounds of this structure type is described by (3, 4, 14). The reported structure details give octahedral sites for  $\text{Al}^{3+}$  and anomalous 7-

coordination for  $\text{Ca}^{2+}$ . Divalent and trivalent ions of the main layer cannot replace each other at their crystallographic positions.

The ionic radii of  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  are very similar. Thus for a replacement of  $\text{Ca}^{2+}$  by  $\text{Cd}^{2+}$  a structure type close to that of the calcium aluminum hydroxide salts (ordered main layers) was expected.

Only with similar radii of trivalent and divalent cations—as in the case of structure type pyroaurite–sjögrenite [3]—a joint replacement on similar crystallographic positions is possible. In this case hexagonal polytypes are crystallizing at elevated temperatures and rhombohedral polytypes at low temperatures.

The aim of the present study was to gain detailed information on the incorporation and crystallochemical fixation of  $\text{Cd}^{2+}$  in hydration products of the aluminate phase of cements. In this paper the chemical compositions and the properties of some new phases are described.

## 2. EXPERIMENTAL

### 2.1. Synthesis

The synthesis of lamellar cadmium aluminum hydroxide hydrates was made by using  $\text{CdAl}_2\text{O}_4$  (8), which has hydraulic properties (5).  $\text{CdAl}_2\text{O}_4$  was made as follows: Metal pieces of Al were dissolved in concentrated  $\text{HNO}_3$ . After addition of  $\text{CdCO}_3$  the solution was evaporated. At  $\approx 600^\circ\text{C}$   $\text{NO}_x$  was volatilized. After grinding the brown powder was heated in a sealed platinum tube at  $950^\circ\text{C}$  for 16 hr. After a second grinding the sample was heated at  $1170^\circ\text{C}$  for 18 hr. A white powder of pure  $\text{CdAl}_2\text{O}_4$  was obtained.

Synthesis of the lamellar cadmium aluminum hydroxide hydrates was carried out by mixing molar proportions of  $\text{CdAl}_2\text{O}_4$ ,  $\text{CO}_3^{2-}$ -free  $\text{Cd}(\text{OH})_2$ , and anion-bearing compounds of cadmium ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{CdCO}_3$ ,  $\text{CdCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and  $\text{H}_2\text{O}$  with water/solid ratio of 7–10. The mixtures were placed in sealed polyethylene bottles and shaken continuously at  $25^\circ\text{C}$  for at least 12 months.

TABLE 1  
Chemical Analysis of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$

	CdO	$\text{Al}_2\text{O}_3$	$\text{SO}_3$	$\text{H}_2\text{O}$	$\Sigma$
wt%	58.6	11.4	9.2	20.5	99.7

## 2.2. Chemical and Physical Characterization

After reaction the precipitates were filtrated in a glove box to avoid contamination by  $\text{CO}_2$ .

All precipitates were examined at 100% r.h. (relative humidity) and 35% r.h. by X-ray powder diffraction analysis using  $\text{CuK}\alpha$  radiation. Si ( $a_0 = 5.4308 \text{ \AA}$ ) was added as internal standard. The lattice parameters were refined by least squares methods.

Thermal and chemical analysis were made from samples dried at 35% relative humidity.

Solids and filtrates were analyzed chemically. CdO and  $\text{Al}_2\text{O}_3$  were determined by AAS.  $\text{SO}_4^{2-}$  content was measured by nephelometric and gravimetric methods,  $\text{CO}_3^{2-}$  by gravimetric and thermogravimetric methods,  $\text{Cl}^-$  volumetrically according to Volhard or ion selective electrode,  $\text{NO}_3^-$  by ion chromatography, and  $\text{H}_2\text{O}$  by thermogravimetry. Infrared absorption spectra between 4000 and  $250 \text{ cm}^{-1}$  were recorded using KBr pellets.

The dehydration and decomposition of the lamellar hydrates was examined using TGA, DSC, and additional XRD high-temperature measurements (up to  $250^\circ\text{C}$ ).

Further information such as crystal shape and irregular forms of the precipitates was obtained by SEM.

## 3. RESULTS

### 3.1. $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot n\text{H}_2\text{O}$

After a reaction time of 13 months at  $25^\circ\text{C}$  a monomineralic precipitate was obtained consisting of small hexagonal platelets with diameters  $\leq 3 \mu\text{m}$ . The pH values of the mother liquid ranged between 5.9 and 6.2 depending on the chosen water/solid ratio.

The composition at 35% r.h., derived from chemical analysis given in Table 1, can be formulated to  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$ . From the XRD pattern (Fig. 1) a hexagonal primitive unit cell with parameters  $a_0 = 5.672 \text{ \AA}$  and  $c_0 = 16.467 \text{ \AA}$  can be calculated. One unit cell is built up by two layers of  $[\text{Cd}_2\text{Al}(\text{OH})_6]^+[\frac{1}{2}\text{SO}_4 \cdot 2\text{H}_2\text{O}]^-$  with layer thicknesses  $c'$  of  $8.234 \text{ \AA}$ . The  $\text{SO}_4^{2-}$  groups seem to be distributed statistically over several interlayers. The X-ray powder data at 100% r.h. and 35% r.h. are given in Fig. 1 and Table 2.

At relative humidities  $\geq 76\%$  the layer thickness is increased to  $10.904 \text{ \AA}$  according to the uptake of some additional water molecules in the interlayers. From thermogravimetric investigations of this higher hydrate, a wa-

TABLE 2  
X-Ray Powder Data of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot n\text{H}_2\text{O}$

$3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 14\text{H}_2\text{O}$ $a_0 = 5.696 \text{ \AA}$ , $c_0 = 3c' = 32.713 \text{ \AA}$ (100% r.h./ $25^\circ\text{C}$ ) SG: $P3_1$ , $P\bar{3}$			$3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$ $a_0 = 5.672 \text{ \AA}$ , $c_0 = 2c' = 16.467 \text{ \AA}$ (35% r.h./ $25^\circ\text{C}$ ) SG: $P3_1$ , $P\bar{3}$		
$d_{\text{exp}} (\text{ \AA})$	$hkl_0$	$hkl$	$d_{\text{exp}} (\text{ \AA})$	$hkl_0$	$hkl$
10.91	100	0 0 3	8.23	100	0 0 2
5.45	50	0 0 6	4.913	<1	1 0 0
3.635	35	0 0 9	4.116	35	0 0 4
2.848	2	1 1 0	3.661	<1	1 0 3
2.838	<1	1 1 1	2.836	2	1 1 0
2.806	<1	1 1 2	2.794	1	1 1 1
2.755	<1	1 1 3	2.745	1	0 0 6
2.727	1	0 0 12	2.681	1	1 1 2
2.690	<1	1 1 4	2.520	<1	1 1 3
2.611	<1	1 1 5	2.456	<1	2 0 0
2.525	<1	1 1 6	2.429	<1	2 0 1
2.432	<1	1 1 7	2.396	<1	1 0 6
2.337	<1	1 1 8	2.336	1	1 1 4
2.242	<1	1 1 9	2.122	<1	1 0 7
2.181	2	0 0 15	2.058	<1	0 0 8
2.147	<1	1 1 10	1.9721	1	1 1 6
2.058	<1	1 1 11	1.7143	<1	1 0 9
1.9693	2	1 1 12	1.6662	<1	1 1 8
1.8856	<1	1 1 13	1.6375	1	3 0 0
1.8175	2	0 0 18	1.6060	<1	3 0 2
1.7314	1	1 1 15	1.5217	<1	3 0 4
1.6442	1	3 0 0			
1.6263	<1	3 0 3			
1.5742	<1	3 0 6			
1.5575	<1	0 0 21			
1.5322	<1	1 1 18			
1.4981	<1	3 0 9			
1.4735	<1	1 1 19			

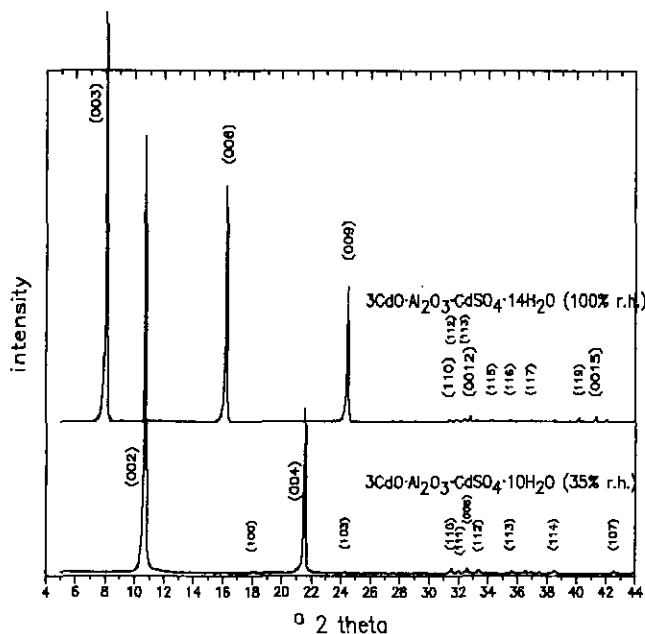


FIG. 1. XRD Pattern of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot n\text{H}_2\text{O}$ : (above), at 100% r.h./ $25^\circ\text{C}$ ,  $n = 14$ ; (below) at 35% r.h./ $25^\circ\text{C}$ ,  $n = 10$ .

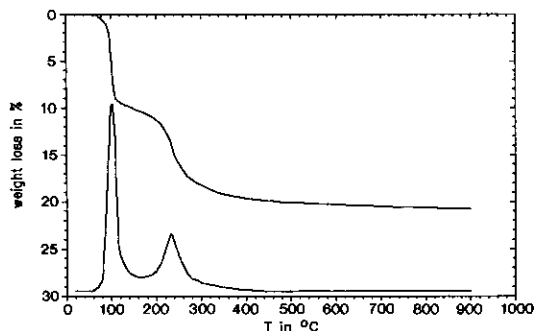


FIG. 2. TGA curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$ : heating rate,  $1^\circ\text{C}/\text{min}$  (TG);  $10^\circ\text{C}/\text{min}$  (DTG); recorded in  $\text{N}_2$ -atmosphere at 35% relative humidity.

ter content of approximately 14  $\text{H}_2\text{O}$  per formula unit can be derived.

Thermoanalysis and XRD high-temperature measurements (Figs. 2–4; Table 3) of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$  indicate that the interlayer water is removed in the range of  $105\text{--}110^\circ\text{C}$  in one single step. Beyond  $160^\circ\text{C}$ ,  $\text{Cd}_2\text{Al}(\text{OH})_6 \cdot \frac{1}{2}\text{SO}_4$  becomes X-ray amorphous due to the removal of some structurally necessary water of the main layer.

IR spectra of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$  obviously show a splitting of the  $\nu_3\text{-SO}_4^{2-}$  vibration into a triplet and an additional vibration  $\nu_1\text{-SO}_4^{2-}$  (Fig. 5; Table 4). According to (1) this fact indicates a monoclinic or triclinic symmetry of the  $\text{SO}_4^{2-}$  group.

### 3.2. $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot n\text{H}_2\text{O}$

A mixture of 6 mmol  $\text{CdAl}_2\text{O}_4$ , 6 mmol  $\text{CdCl}_2$ , and 12 mmol  $\text{Cd}(\text{OH})_2$  with 30 ml  $\text{H}_2\text{O}$  was shaken continuously for 12 months. After reaction the value of pH of the mother liquid is 6.8. The resulting precipitate consists of pseudo-hexagonal platelets with diameters  $\leq 1 \mu\text{m}$ . From chemi-

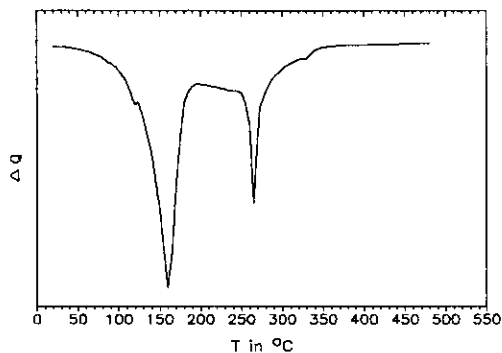


FIG. 3. DSC curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$ : heating rate,  $10^\circ\text{C}/\text{min}$ .

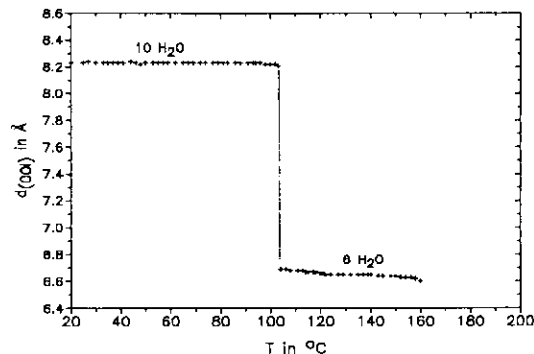


FIG. 4.  $d_{(001)}$  of dehydration stages of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$  recorded by XRD measurements at elevated temperatures.

cal analysis of a sample dried at 35% r.h. the following formula can be calculated:  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$  (Table 5).

From the XRD pattern (Fig. 20) a monoclinic pseudo-hexagonal unit cell (Table 6) was calculated. At 100% r.h. and 35% r.h. the same cell parameters were detected.

DSC and TGA curves (Figs. 6 and 7) indicate a removal of the interlayer water in several steps. With increasing temperature exceeding  $200^\circ\text{C}$  the decomposition of the main layers takes place (Table 7).

At  $62 \pm 2^\circ\text{C}$  a reversible phase transformation was detected. The monoclinic hydrate  $10\text{H}_2\text{O}$  turns into a lower hydrate of rhombohedral symmetry (Fig. 8), with the cell parameters given in Table 8. By thermogravimetry the water content of this hydrate can be determined to be 9  $\text{H}_2\text{O}$ . The IR spectroscopical data are given in Fig. 9 and Table 9.

### 3.3. $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot n\text{H}_2\text{O}$

“Cadmium-monocarboaluminate”  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot n\text{H}_2\text{O}$  could be synthesized without additional ions

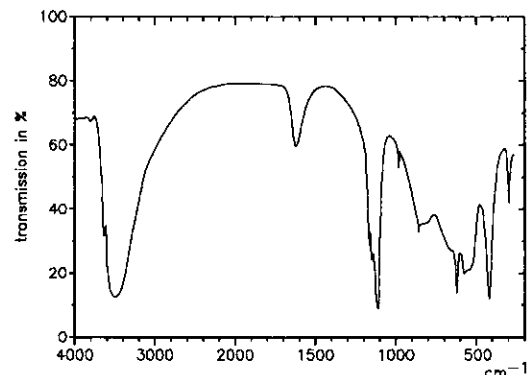


FIG. 5. IR spectrum of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$ .

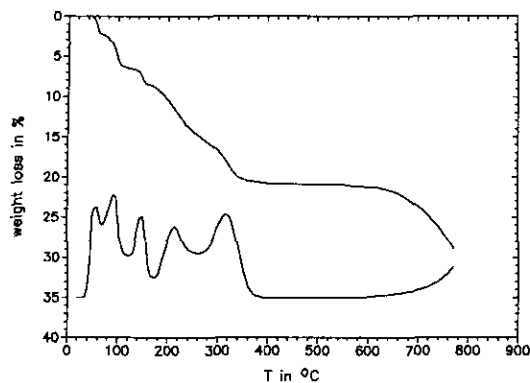


FIG. 6. TGA curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$ : heating rate,  $2^\circ\text{C}/\text{min}$  (TGA);  $5^\circ\text{C}/\text{min}$  (DTG).

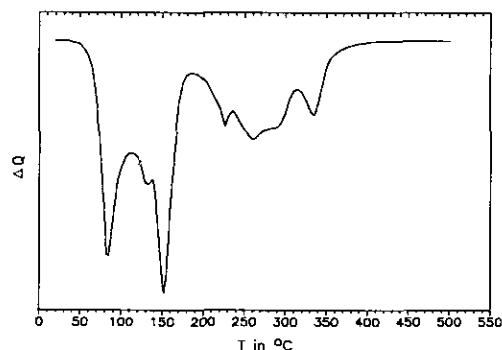


FIG. 7. DSC curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$ : heating rate,  $10^\circ\text{C}/\text{min}$ .

TABLE 3  
Thermal Weight Loss, Water Content and Corresponding  $d_{(001)}$  Values of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$

$T$ ( $^\circ\text{C}$ )	wt. loss (%)	Water cont.	$d_{(001)}$ ( $\text{\AA}$ )
25	—	10	8.23
105	8.4	6	6.25
		destruction of the structure	
270	17.6		
500	20.3		
900	20.5		

TABLE 4  
IR Vibrations of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot 10\text{H}_2\text{O}$

300, 420	Cd—O vibr.
530–580, 620, 860	Al—O vibr. and metal—OH vibr.
980	$\nu_1\text{—SO}_4^{2-}$ vibr.
1110, 1150, 1165	$\nu_3\text{—SO}_4^{2-}$ (split into triplet)
1625	$\nu_2\text{—H}_2\text{O}$ vibr.
3500	$\nu_1/\nu_3\text{—H}_2\text{O}$ vibr. (interlayer water)
3630	OH vibr. (main layer)

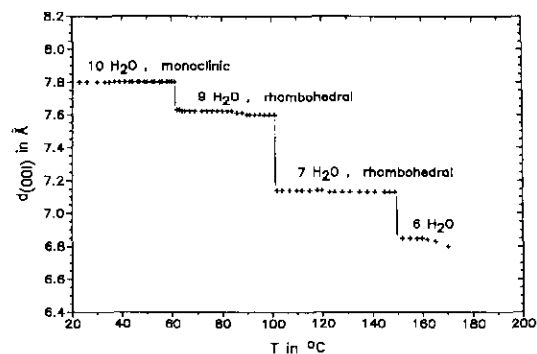


FIG. 8. Course of  $d_{(001)}$  values of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$ : recorded by XRD measurements at elevated temperatures.

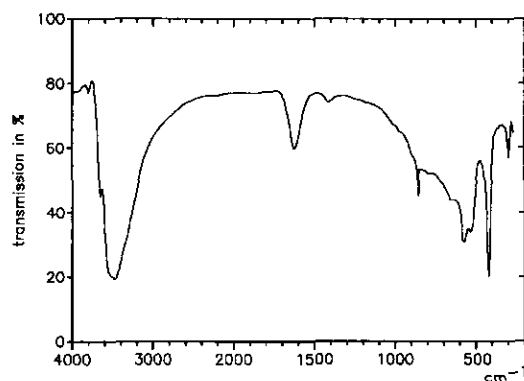


FIG. 9. IR spectrum of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$ .

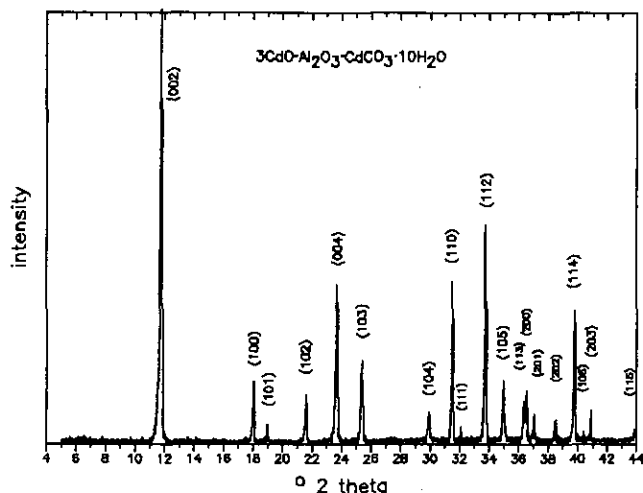


FIG. 10. XRD pattern of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$  ( $25^\circ\text{C}/35\%$  r.h.).

TABLE 5  
Chemical Analysis of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$  (35% r.h.)

	CdO	$\text{Al}_2\text{O}_3$	$\text{Cl}_2$	$\text{H}_2\text{O}$	$\Sigma$
wt%	59.6	11.6	8.2	20.9	100.3

TABLE 6  
X-ray Powder Data of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$

$d_{\text{exp}}$ (Å)	$I/I_0$	$hkl$	$d_{\text{exp}}$ (Å)	$I/I_0$	$hkl$	$d_{\text{exp}}$ (Å)	$I/I_0$	$hkl$
7.80	100	0 0 2	2.531	1	3 1 2	1.9501	1	0 0 8
4.815	4	2 0 0	2.500	2	0 2 3	1.9213	3	0 2 6
4.787	6	-1 1 1	2.453	5	2 2 0	1.9167	1	-4 0 6
4.581	1	1 1 1			-2 2 1	1.9106	<1	-2 0 8
4.405	1	-2 0 2	2.429	1	-3 1 4	1.8671	1	-3 1 7
3.902	25	0 0 4	2.408	3	4 0 0	1.8606	3	2 2 5
3.849	7	2 0 2	2.340	8	3 1 3	1.8402	7	4 2 0
3.714	12	-1 1 3	2.302	7	0 2 4	1.7843	1	5 1 1
3.441	2	1 1 3	2.291	5	2 2 2	1.7720	2	-1 3 3
3.284	<1	-2 0 4	2.234	10	-3 1 5	1.7431	2	-4 2 4
2.851	10	0 2 0	2.203	3	-4 0 4	1.7202	<1	2 0 8
2.819	30	-3 1 1	2.153	3	-2 2 4			2 2 6
2.730	9	-1 1 5	2.144	<1	3 1 4	1.7022	<1	-1 3 4
2.693	12	3 1 1	2.091	3	-1 1 7	1.6752	<1	4 2 3
2.678	10	0 2 2	2.043	<1	-3 1 6	1.6510	2	5 1 3
2.611	7	-3 1 3	2.009	8	2 2 4	1.6401	8	-3 3 1
2.600	1	0 0 6	1.9733	2	1 1 7	1.6218	3	-1 3 5
2.547	2	1 1 5	1.9596	3	3 1 5			-6 0 2

Note.  $a_0 = 9.746$  Å,  $b_0 = 5.703$  Å,  $c_0 = 15.783$  Å,  $\beta = 98.65^\circ$ , SG, C2/C.

by a 12 month paste reaction of stoichiometric proportions of  $\text{Cd}(\text{OH})_2$ ,  $\text{CdAl}_2\text{O}_4$ , and  $\text{CdCO}_3$  with water (w/s ratio 7–10). The resulting pH of the mother liquid ranged between 8.5 and 9.1 depending on w/s ratio.

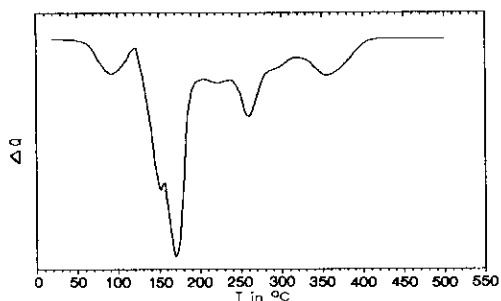


FIG. 11. DSC curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$  ( $10^\circ\text{C}/\text{min}$ ).

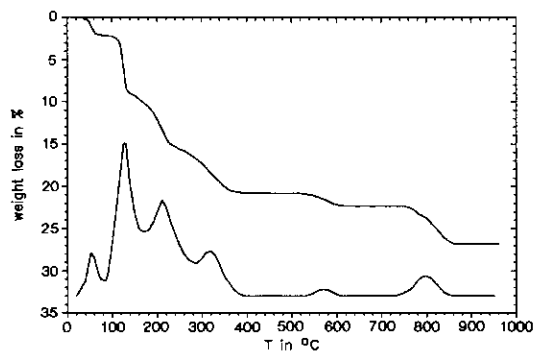


FIG. 12. TGA curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$ : heating rate,  $1^\circ\text{C}/\text{min}$  (TG);  $5^\circ\text{C}/\text{min}$  (DTG);  $\text{N}_2$  atmosphere (35% r.h.).

From the XRD pattern a hexagonal primitive unit cell could be derived containing two layers of  $[\text{Cd}_2\text{Al}(\text{OH})_6]^{+}[\frac{1}{2}\text{CO}_3 \cdot n\text{H}_2\text{O}]^{-}$ . At room temperature the water content of the interlayer is dependent on relative humidity. At 35% r.h. Cadmium-monocarboaluminate has the composition  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$  (Table 10) with cell constants  $a_0 = 5.675$  Å,  $c_0 = 2c' = 15.021$  Å

TABLE 7  
Thermal Weight Loss of  
 $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$

$T$ ( $^\circ\text{C}$ )	wt. loss (%)	Water content
25	—	10
65	2.2	9
105	6.2	7
155	8.4	6
240	13.8	decomposition of the mainlayers;
350	20.3	volatilization of
500	20.9	Cl-bearing compounds
>550		

TABLE 8  
Dehydration Stages of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$

$T$ ( $^\circ\text{C}$ )	$\text{H}_2\text{O}$ content	$d_{(001)}$ (Å)	Cell parameter (Å)
25	10	7.80	$a_0 = 9.746$ , $b_0 = 5.703$ , $\beta = 98.65$ , $c_0 = 15.783$ , $c' = 7.802$ ,
62	9	7.61	$a_0 = 5.682$ , $c_0 = 6c' = 45.678$ , rhombohedral
102	7	7.14	$a_0 = 5.677$ , $c_0 = 6c' = 42.817$ , rhombohedral
150	6	6.85	$c' \approx 6.85$

TABLE 9  
IR Vibrations of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot 10\text{H}_2\text{O}$

Wavenumber ( $\text{cm}^{-1}$ )	Vibrations
300, 420	Cd—O vibr.
535, 580, 660, 860	Al—O vibr. and metal—OH vibr.
1410	weak $\nu_3\text{—CO}_3^{2-}$ vibr., caused by preparation
1625	$\nu_2\text{—H}_2\text{O}$ vibr.
3470–3560	$\nu_1/\nu_3\text{—H}_2\text{O}$ vibr. (interlayer water)
3640	OH vibr. (main layer)

(Fig. 10, Table 11). At relative humidities exceeding 35% uptake of additional water molecules in the interlayers occurs and  $c_0$  is increased to  $15.128 \text{ \AA}$  ( $= 2c'$ ) whereas  $a_0$  remains approximately constant ( $5.674 \text{ \AA}$ ). By thermogravimetry the water content of that higher hydration stage was determined to be 11–12 $\text{H}_2\text{O}$ .

The XRD pattern does not show any additional reflections, which could indicate a superstructure in the crystallographic direction  $c$ . Thus a statistical distribution of  $\text{CO}_3^{2-}$  groups in the interlayers must be assumed.

Up to  $500^\circ\text{C}$  the DSC curve shows five endotherms (Fig. 11). By TGA and XRD high-temperature measurements (Figs. 12 and 13) two lower hydrates (9  $\text{H}_2\text{O}$  with  $c' = 7.43 \text{ \AA}$  and 6  $\text{H}_2\text{O}$  with  $c' = 6.32 \text{ \AA}$ ) were distinguished. At about  $750^\circ\text{C}$   $\text{CO}_2$  is released. Thermal weight loss is summarized in Table 12.

IR spectra of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$  (Fig. 14) show a slight asymmetry of the  $\nu_3\text{—CO}_3^{2-}$  vibration possibly due to a splitting of  $\nu_3$ . Additional appearance of a very weak  $\nu_1\text{—CO}_3^{2-}$  vibration at  $1055 \text{ cm}^{-1}$  indicates

TABLE 10  
Chemical Analysis of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$  (35% r.h.)

	CdO	$\text{Al}_2\text{O}_3$	$\text{CO}_2$	$\text{H}_2\text{O}$	$\Sigma$
wt%	61.2	11.8	5.3	21.5	99.8

somewhat distorted  $\text{CO}_3^{2-}$  groups caused by hydrogen bonding (Table 13).

### 3.4. $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$

Synthesis of this compound was made by mixing molar proportions of  $\text{Cd}(\text{OH})_2$ ,  $\text{CdAl}_2\text{O}_4$ , and  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with water ( $w/s \approx 8$ ). After a reaction time of 12 months the mother liquid was at a pH value of 6.6. From XRD measurements (Fig. 15) at 100% r.h. and 35% r.h. the following cell constants could be derived:  $a_0 = 5.689 \text{ \AA}$ ;  $c_0 = c' = 16.535 \text{ \AA}$  (Table 14). The chemical analysis is given in Table 15, and the DSC curve is shown in Fig. 16.

The XRD pattern shows additional basal reflections indicating a superstructure in crystallographic direction  $c$ . Probably every unit cell is composed of two main layers  $[\text{Cd}_2\text{Al}(\text{OH})_6]^+$  and two interlayers  $[\text{NO}_3 \cdot n\text{H}_2\text{O}]^-$ . Presumably the latter are ordered in two different manners. Special orientations of the  $\text{NO}_3^-$  groups could cause the superstructure.

By thermoanalytical investigations up to  $70^\circ\text{C}$  three lower hydration stages could be detected (Fig. 17; Table 16). At about  $200^\circ\text{C}$  decomposition of the main layers starts.

Figure 18 shows the course of  $d_{(001)}$  values made by XRD measurements at elevated temperatures. In XRD

TABLE 11  
X-Ray Powder Data of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$

$d_{\text{exp}}$ ( $\text{\AA}$ )	$hkl$	$d_{\text{exp}}$ ( $\text{\AA}$ )	$hkl$	$d_{\text{exp}}$ ( $\text{\AA}$ )	$hkl$
7.51	100	2.335	4	1.6383	10
4.916	8	2.264	25	1.6166	2
4.674	<1	2.231	<1	1.6006	12
4.113	7	2.206	2	1.5801	8
3.756	30	2.062	2		109
3.508	14	2.056	3	1.5661	1
2.984	5	1.9669	10	1.5016	5
2.838	25	1.9023	10	1.4383	<1
2.789	<1	1.8776	9	1.4188	3
2.654	35	1.8578	4	1.4048	5
2.564	9	1.8437	1	1.3941	4
2.469	5	1.8034	5	1.3808	1
2.458	7	1.7415	4	1.3711	<1
2.426	5	1.6651	1	1.3630	<1

Note.  $a_0 = 5.675 \text{ \AA}$ ,  $c_0 = 2c' = 15.021$ , SG,  $P3$ ,  $P3$ .

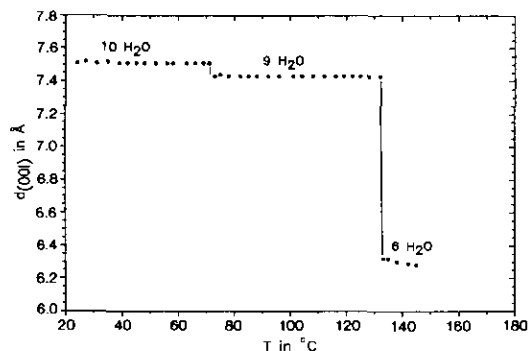


FIG. 13. Course of  $d_{(001)}$  values of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$ : XRD measurements at elevated temperatures.

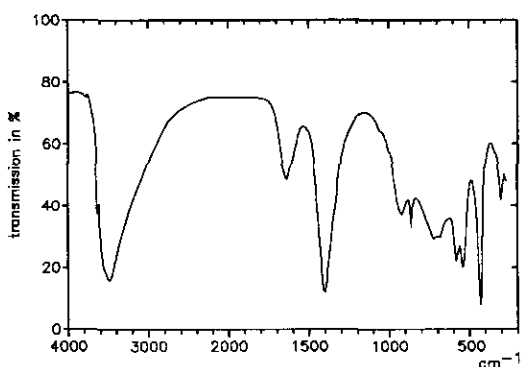


FIG. 14. IR spectrum of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$ .

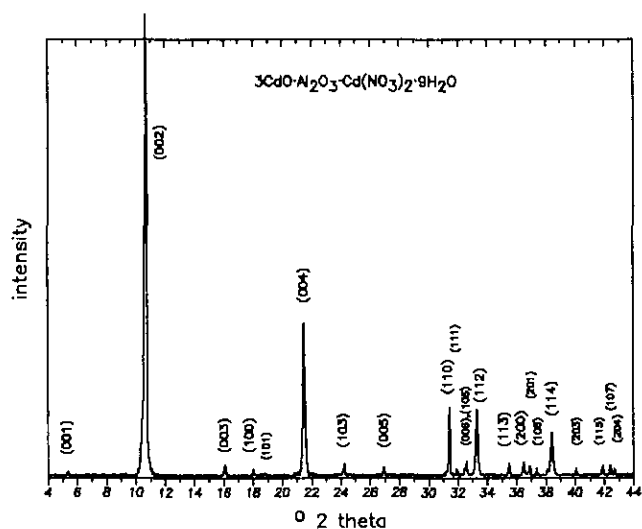


FIG. 15. XRD pattern of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ .

patterns of the lower hydrates no additional reflections indicating a superstructure are visible. In Table 17 the determined cell constants are listed.

Between  $70^\circ\text{C}$  and  $200^\circ\text{C}$  the lowest hydration stage  $\text{Cd}_2\text{Al}(\text{OH})_6 \cdot \text{NO}_3$  is stabilized. The XRD pattern of

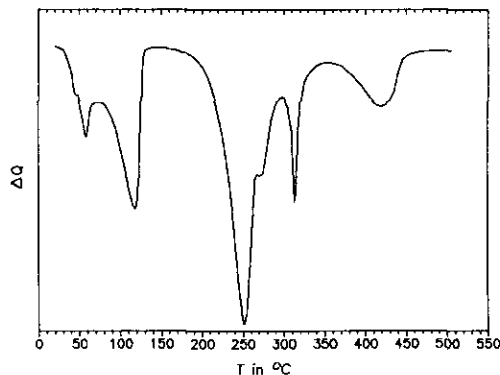


FIG. 16. DSC curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ .

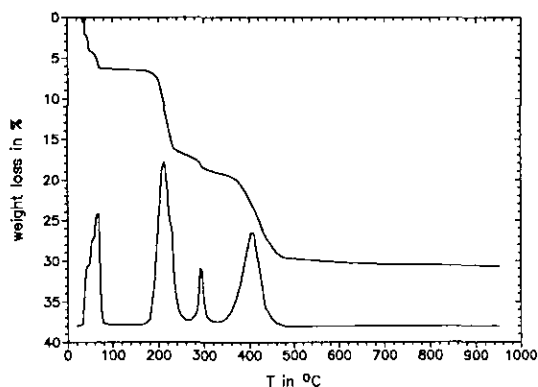


FIG. 17. TGA curve of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ : heating rate,  $1^\circ\text{C}/\text{min}$  (TGA);  $5^\circ\text{C}/\text{min}$  (DTG).

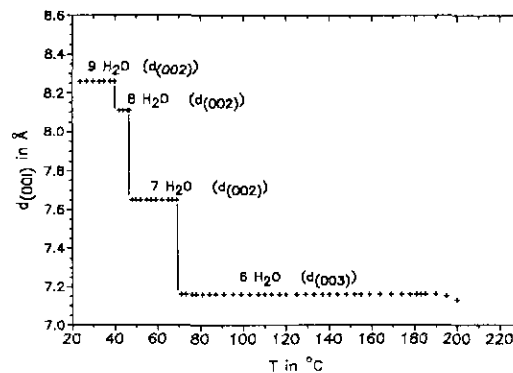


FIG. 18. Course of  $d_{(001)}$  values of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ .

$\text{Cd}_2\text{Al}(\text{OH})_6 \cdot \text{NO}_3$  could be indexed completely only with the assumption of a hexagonal primitive unit cell with  $c_0 = 3c'$ .

IR spectroscopical data of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  are given in Fig. 19 and Table 18.

TABLE 12  
Thermal Weight Loss, Water Content, and Corresponding  $d_{(001)}$   
Values of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$

$T$ ( $^{\circ}\text{C}$ )	wt. loss (%)	Water content	$d_{(001)}$ ( $\text{\AA}$ )
25	—	10	7.51
70	2.2	9	7.43
135	8.7	6	6.32
230	15.1	loss of water and decomposition of main layers	
370	20.6		
600	22.2		
800	26.8	decarbonization	

TABLE 13  
IR Vibrations of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot 10\text{H}_2\text{O}$

Wave number ( $\text{cm}^{-1}$ )	Vibrations
300, 425	Cd—O vibr.
540, 580, 680–720, 860, 920	Al—O vibr. and metal—OH vibr.
1055	$\nu_1$ — $\text{CO}_3^{2-}$ vibr. (very weak)
1405	$\nu_3$ — $\text{CO}_3^{2-}$ vibr. (slightly asymmetric)
1635	$\nu_2$ — $\text{H}_2\text{O}$ vibr.
3480–3560	$\nu_1/\nu_3$ — $\text{H}_2\text{O}$ vibr. (interlayer water)
3630	OH vibr. (main layer)

#### 4. STRUCTURAL INFORMATION

On the basis of a crystal structure determination by Terzis *et al.* (14) of the lamellar calcium aluminum chloride hydrate, "Friedel's salt"  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+ [\text{Cl} \cdot 2\text{H}_2\text{O}]^-$ , the atomic positions of Ca were replaced

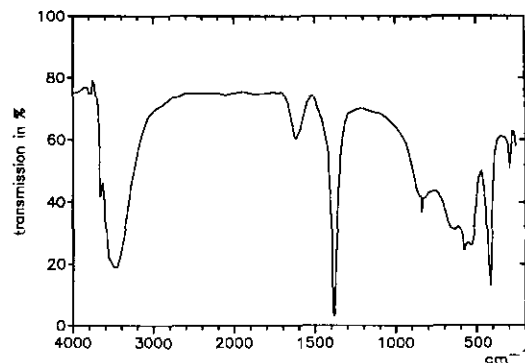


FIG. 19. IR spectrum of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ .

by Cd and the X-ray pattern was calculated. Calculation was carried out by using the program MICROPOWD (17) with atomic positions in analogy to crystal structure data of  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+ [\text{Cl} \cdot 2\text{H}_2\text{O}]^-$  and supposed  $B_{\text{iso}} = 1$ .

A comparison of the measured X-ray lines and the calculated pattern is shown in Fig. 20. The two patterns are approximately congruent.

On the basis of this calculated pattern a schematic structural model with different polyhedra was constructed using the program ATOMS (16). In Fig. 21 the different atomic arrangements are demonstrated. The octahedral polyhedra are due to  $\text{Al}(\text{OH})_6$  and the irregular 7th neighbor of Cd is an oxygen atom from a water molecule of the interlayer. In analogy to "Friedel's salt" the minilayers are ordered. Within the hydroxide layer Cd and Al are situation in octahedral cavities in an ordered way. Like in the crystal structure of  $[\text{Ca}_2\text{Al}(\text{OH})_6][\text{Cl} \cdot 2\text{H}_2\text{O}]$ , presumably the interlayers  $[\text{Cl} \cdot 2\text{HO}]^-$  (Fig. 21: Cl, dark,  $\text{H}_2\text{O}$ , white) of the analogous Cd compound are ordered too.

TABLE 14  
X-ray Powder Data of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$

$d_{\text{exp}}$ ( $\text{\AA}$ )	$I/I_0$	$hkl$	$d_{\text{exp}}$ ( $\text{\AA}$ )	$I/I_0$	$hkl$	$d_{\text{exp}}$ ( $\text{\AA}$ )	$I/I_0$	$hkl$
16.54	<1	0 0 1	2.463	2	2 0 0	1.8175	<1	1 1 7
8.27	100	0 0 2	2.436	1	2 0 1	1.7647	<1	2 1 3
5.51	2	0 0 3	2.406	1	1 0 6	1.6718	<1	1 1 8
4.924	1	1 0 0	2.360	<1	2 0 2	1.6423	4	3 0 0
4.721	<1	1 0 1	2.343	10	1 1 4	1.6223	<1	2 1 5
4.133	30	0 0 4	2.249	<1	2 0 3	1.6109	5	3 0 2
3.673	2	1 0 3	2.156	2	1 1 5	1.5835	<1	2 0 8
3.307	1	0 0 5	2.130	2	1 0 7	1.5433	<1	1 1 9
2.845	10	1 1 0	2.116	<1	2 0 4			/2 1 6
2.802	<1	1 1 1	1.9795	5	1 1 6	1.5262	2	3 0 4
2.757	1	0 0 6	1.9061	<1	1 0 8	1.4725	<1	2 0 9
2.746	2	1 0 5	1.8620	<1	2 1 0	1.4625	<1	2 1 7
2.690	14	1 1 2	1.8503	<1	2 1 1	1.4223	1	2 2 0
2.529	2	1 1 3	1.8367	1	2 0 6	1.4018	2	2 2 2

Note.  $a_0 = 5.689 \text{ \AA}$ ,  $c_0 c' = 16.535 \text{ \AA}$  (superstructure), SG, P3,  $\bar{P}3$ .



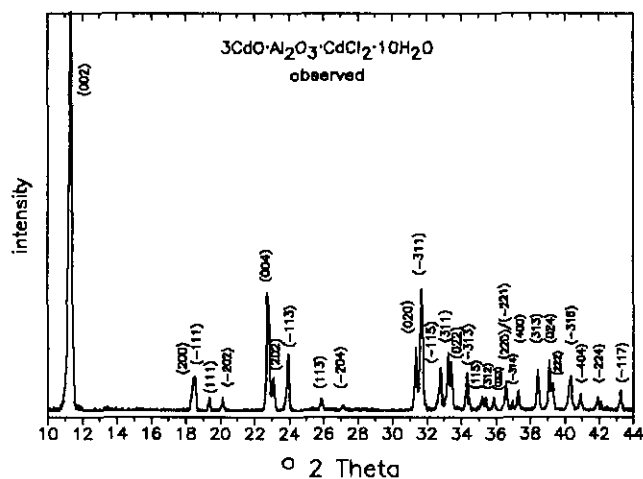
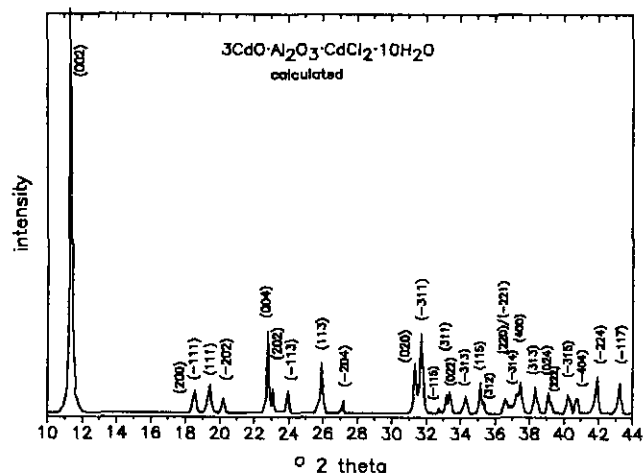


FIG. 20. Measured and calculated X-ray powder patterns of  $[\text{Cd}_2\text{Al}(\text{OH})_6][\text{Cl} \cdot 2\text{H}_2\text{O}]$ .

## 5. DISCUSSION

In the crystal structure type of lamellar calcium aluminum hydroxide salts (e.g., monochloroaluminate, monosulfoaluminate) calcium can be completely replaced by cadmium. The analogous irregular 7-coordinated Cd with the 7th neighbor from the interlayer (O atom of water molecule) could be proved. Like in the lamellar calcium aluminum hydroxide salts, the main layers are ordered

TABLE 15  
Chemical Analysis of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$   
(35% r.h.)

	CdO	$\text{Al}_2\text{O}_3$	$\text{N}_2\text{O}_5$	$\text{H}_2\text{O}$	$\Sigma$
wt%	57.5	11.1	12.5	18.5	99.6

TABLE 16  
Thermal Weight Loss of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$

$T$ ( $^\circ\text{C}$ )	wt. loss (%)	Water content
25	—	9
40	2.2	8
50	4.1	7
70	6.2	6
240	16.4	loss of water and decomposition
300	18.5	of main layer;
470	29.5	exceeding $350^\circ\text{C}$ : $\text{NO}_3^- \rightarrow \text{NO}_2$
950	30.7	

TABLE 17  
 $d_{(001)}$  Values and Cell Parameters of Determined Hydration  
Stages of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$

$T$ ( $^\circ\text{C}$ )	$\text{H}_2\text{O}$ cont.	$d_{(001)}$ ( $\text{\AA}$ )	Cell parameters ( $\text{\AA}$ )
25	9	8.26 ( $d_{(002)}$ )	$a_0 = 5.689$ $c_0 = 16.535 = c'$
40	8	8.10 ( $d_{(002)}$ )	$a_0 = 5.691$ $c_0 = 16.192 = 2c'$
48	7	7.66 ( $d_{(002)}$ )	$a_0 = 5.690$ $c_0 = 15.316 = 2c'$
70	6	7.15 ( $d_{(003)}$ )	$a_0 = 5.684$ $c_0 = 21.455 = 3c'$

and the ratio of Ca : Al is fixed to 2 : 1. The cell constant  $a_0$  ranges between 5.67 and 5.70  $\text{\AA}$ . This is about  $\sqrt{3}$  times the value of  $a_0$  of the  $\text{Cd}(\text{OH})_2$  structure. The layer thickness  $c'$  is dependent on the size of the interlayer anion and water content.

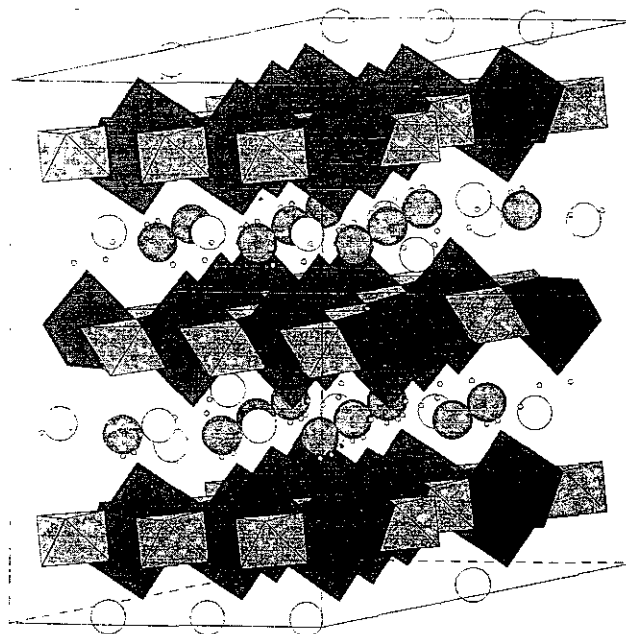


FIG. 21. Crystal structure of  $[\text{Cd}_2\text{Al}(\text{OH})_6]^+ [\text{Cl} \cdot 2\text{H}_2\text{O}]^-$  based on the crystal structure determination of isostructural "Friedel's salt" (14).

TABLE 18  
IR Vibrations of  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$

Wavenumber ( $\text{cm}^{-1}$ )	Vibrations
300, 420	Cd-O vibr.
520, 580,	Al-O vibr. and
620-660, 840	metal-OH vibr.
1380	$\nu_3$ - $\text{NO}_3$ vibr.
1620	$\nu_2$ - $\text{H}_2\text{O}$ vibr.
3490	$\nu_1/\nu_3$ - $\text{H}_2\text{O}$ vibr. (interlayer water)
3650	OH vibr. (main layer)

Compared to cell constant  $a_0$  of lamellar calcium aluminum hydroxide salts ( $a_0 \approx 5.75 \text{ \AA}$ ) the values  $a_0$  of the lamellar cadmium salts are generally about 0.50–0.1  $\text{\AA}$  lower. Presumably this fact is not only due to the very little difference between the ionic radii of Ca and Cd but more to the higher polarizability of Cd.

The different water contents are due to the interlayer anion, temperature and relative humidity. The following hydration stages were distinguished:  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdSO}_4 \cdot n\text{H}_2\text{O}$  ( $n = 14, 10, 6$ ),  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCl}_2 \cdot n\text{H}_2\text{O}$  ( $n = 10, 9, 7, 6$ ),  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CdCO}_3 \cdot n\text{H}_2\text{O}$  ( $n = 11-12, 10, 9, 6$ ),  $3\text{CdO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cd}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  ( $n = 9, 8, 7, 6$ ).

The compounds discussed in this paper also can be synthesized by precipitation methods (5). The phases are precipitating with bad crystallinity very immediately at pH values around 10. Because of their quick crystallization, low solubility, and high potential for immobile crystallochemical fixation of Cd, applications to environmental technology seem to be possible (e.g., purification of industrial sewages).

As described in (5) partial solid solution between lamellar cadmium and calcium aluminum hydroxide salts ex-

ists. During hydration reactions of a cementitious binder such solid solutions (or pure Cd salts discussed in this paper) could easily be formed and lead to a complete fixation of cadmium.

Finally it is to be mentioned that this paper partially contains some of the results of a more extensive investigation on stabilization and immobilization of potentially hazardous wastes using cementitious materials.

#### ACKNOWLEDGMENTS

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