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Thermal stability of basic aluminum sulfate [1]

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Abstract

The tridecameric aluminum polymer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ is prepared by forced hydrolysis of an $Al(NO_3)_3$ solution by NaOH up to an OH:Al mol ratio of 2.2. Upon addition of sulfate the tridecamer crystallizes into macroscopic crystallites of the basic aluminum sulfate $Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}$, which is characterized structurally by means of X-ray diffraction, ^{27}Al solid-state magic angle spinning NMR, IR and chemically by inductively coupled plasma atomic emission spectroscopy. The basic aluminum sulfate has a monoclinic unit cell with $a = 20.188 \pm 0.045$ Å, $b = 11.489 \pm 0.026$ Å, $c = 24.980 \pm 0.056$ Å, and $\beta = 102.957 \pm 0.022°$. With TG analysis, DTA and heating stage X-ray diffraction the thermal decomposition is studied. The tridecamer persists as a stable unit in the sulfate structure to temperatures of 80°C. Approximately 9 mol H_2O are adsorbed in excess per one mol basic aluminum sulfate; these are easily lost by heating to 80°C. From 80 to 360°C the tridecamer unit will gradually decompose losing its 12 water and 24 hydroxyl groups, to finally become X-ray amorphous. From 360 to 950°C, with a maximum between 880 and 950°C, SO_3 is removed, leaving behind primary aluminum oxide.

INTRODUCTION

Forced hydrolysis of aluminum solutions by addition of alkali hydroxide solutions results in the formation of the tridecamer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ [1, 2]. The tridecamer contains a central tetrahedral AlO_4 unit in a cage of twelve aluminum octahedrals. The tridecamer is of commercial interest because of its antiperspirant activity, its ability to control viscosity of kaolinite clays [3] and its pillaring capacity in smectites to form

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molecular sieves and catalysts [4–6]. ^{27}Al NMR spectroscopy has confirmed the presence of both octahedral (chemical shift 0 ppm) and tetrahedral aluminum (chemical shift 62.5 ppm) in the tridecameric complex [1, 2, 7, 8].

Johannson [9–11] and Johansson et al. [12] have precipitated two different basic aluminum sulfates, cubic $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_4 \cdot xH_2O$ and monoclinic $[Al_{13}O_4(OH)_{25}(H_2O)_{11}](SO_4)_3 \cdot xH_2O$, both consisting of the tridecameric aluminum polymers attached by hydrogen bonding to the oxygen atoms of the sulfate. Solid-state high-resolution ^{27}Al NMR has confirmed the presence of both tetrahedral [13, 14] and octahedral aluminum in basic aluminum salts [15, 16].

Until now the basic aluminum sulfate has only been characterized by means of X-ray diffraction (XRD) and ^{27}Al solid-state magic angle spinning (MAS) NMR. In this study basic aluminum sulfate, precipitated from partly hydrolyzed aluminum nitrate solutions, is characterized with ^{27}Al solid-state MAS NMR spectroscopy, XRD, IR spectroscopy and is chemically analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Thermal decomposition behavior is studied by TG analysis, DTA, and heating-stage X-ray diffraction (HT-XRD). This study of the thermal decomposition will help towards a better understanding of the processes that take place during calcination of smectites pillared with the tridecameric polymer.

EXPERIMENTAL TECHNIQUES

Tridecamer solution

The tridecameric aluminum polymer is obtained by hydrolysis of 0.5 M aluminum nitrate solution with a 0.5 M sodium hydroxide solution, until an OH:Al mol ratio of 2.2 is reached. Kloprogge et al. [2] have described the details of the hydrolysis.

5 ml of the tridecamer solution is diluted with 5 ml D_2O before measurements of solution NMR. The ^{27}Al NMR spectra are recorded on a Bruker WP 200 spectrometer operating at 52.148 MHz (4.6 Tesla) at the Department of Organic Chemistry of the University of Utrecht. Chemical shifts are reported in ppm relative to $[Al(H_2O)_6]^{3+}$. Amounts of aluminum species are calculated from the ratios of the peak areas and the peak area of the standard $[Al(H_2O)_6]^{3+}$ with the same total aluminum concentration.

Basic aluminum sulfate

To 100 ml of the tridecamer solution 100 ml of 0.5 M sodium sulfate is added, resulting in final concentrations of 0.085 M Al^{3+} and 0.25 M $(SO_4)^{2-}$. The precipitate is aged for 42 days before removal from the solution for further investigation.

The precipitates grown at the bottom and the walls of the container are collected separately, washed with distilled water and dried at room temperature. Chemical compositions are obtained by dissolving 500 mg of each precipitate in 50 ml 1 M HCl and analyzed for aluminum, sodium and sulfur by ICP-AES. XRD powder patterns are recorded on a Phillips PW 1050/25 diffractometer using Cu Kα radiation. Unit-cell dimensions are calculated using the least-squares refinement computer program UNITCELLC [17]. Heating stage XRD is carried out using an HT Guinier Cu Kα1 (Enraf Nonius FR553) focussing powder camera. The temperature is raised from 35 to 700°C using a heating rate of 10°C h^{-1}. ^{27}Al MAS NMR spectra are recorded on a Bruker WM 500 spectrometer operating at 130.321 MHz (11.7 Tesla) at the Department of Physical Chemistry, Faculty of Science, University of Nijmegen. The sample spin-frequency is approximately 3 kHz. Chemical shifts are reported in ppm relative to $[Al(H_2O)_6]^{3+}$. IR absorption spectra are obtained on powdered samples in KBr tablets with 1 mass% sample concentration using a Perkin Elmer 580 IR spectrophotometer. TG analyses are performed with a Du Pont 1090 thermal analyzer, applying a heating rate of 10°C min^{-1} under a nitrogen flow of 50 ml min^{-1}.

RESULTS

Preparation

The hydrolyzed aluminum solution with an OH:Al ratio of 2.2 contains 27% monomeric aluminum and 73% tridecameric aluminum based on the area ratios of the Al(VI) and Al(IV) NMR resonances at 0.16 ppm and 63.35 ppm, respectively, assuming a 1:12 ratio for the tridecamer (Fig. 1A). Comparison with an external Al^{3+} standard implies that the alumina in the solution was completely recovered, proving that no other aluminum polymer species are present.

Addition of sodium sulfate to the tridecamer solution results, after approximately 15 min, in the steady growth from the clear solution of small needles on the walls of the container. After 1 h the solution becomes cloudy white. Overnight aging results again in a clear solution with approximately 0.5 mm long needles at the wall and a precipitate without any visible crystals at the bottom.

Characterization

ICP-AES analysis of the washed crystals from the wall dissolved in HCl results in an atom ratio of Al:Na:S = 13:0.1:3.55, which can be recalculated to a structural formula of $Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$-$(SO_4)_{3.55} \cdot xH_2O$. The unwashed precipitate of the bottom has an atom

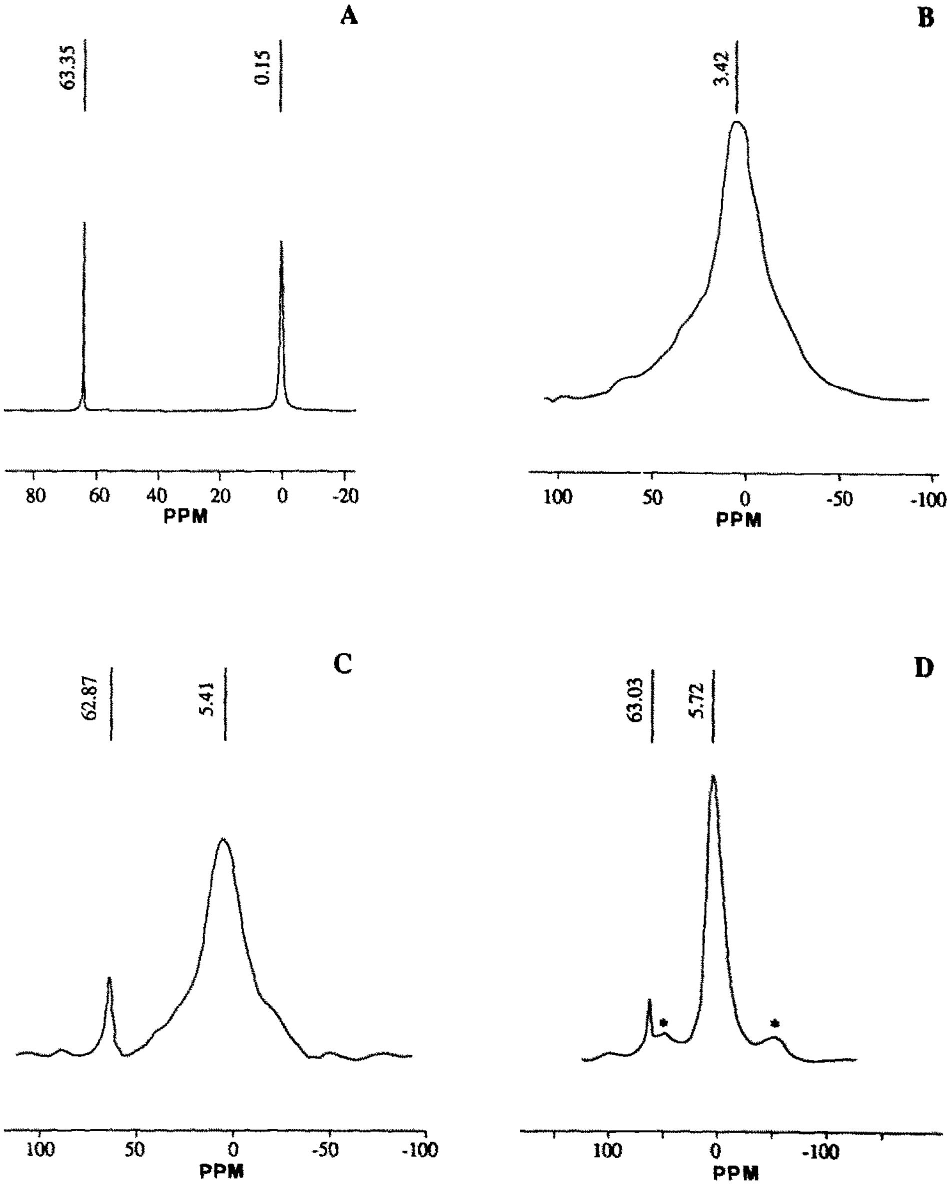


Fig. 1. (A) ^{27}Al NMR spectrum of the partly hydrolyzed solution with an OH:Al ratio of 2.2. ^{27}Al solid-state MAS NMR spectra of (B) the precipitate from the bottom, (C) the unwashed and (D) the washed crystals from the wall.

ratio Al:Na:S = 6:4:2. Upon washing the precipitate completely redissolves.

The XRD pattern of the unwashed bottom precipitate reveals the presence of crystalline $NaNO_3$, while no crystalline basic aluminum sulfate has been observed. The XRD pattern of the crystals from the wall

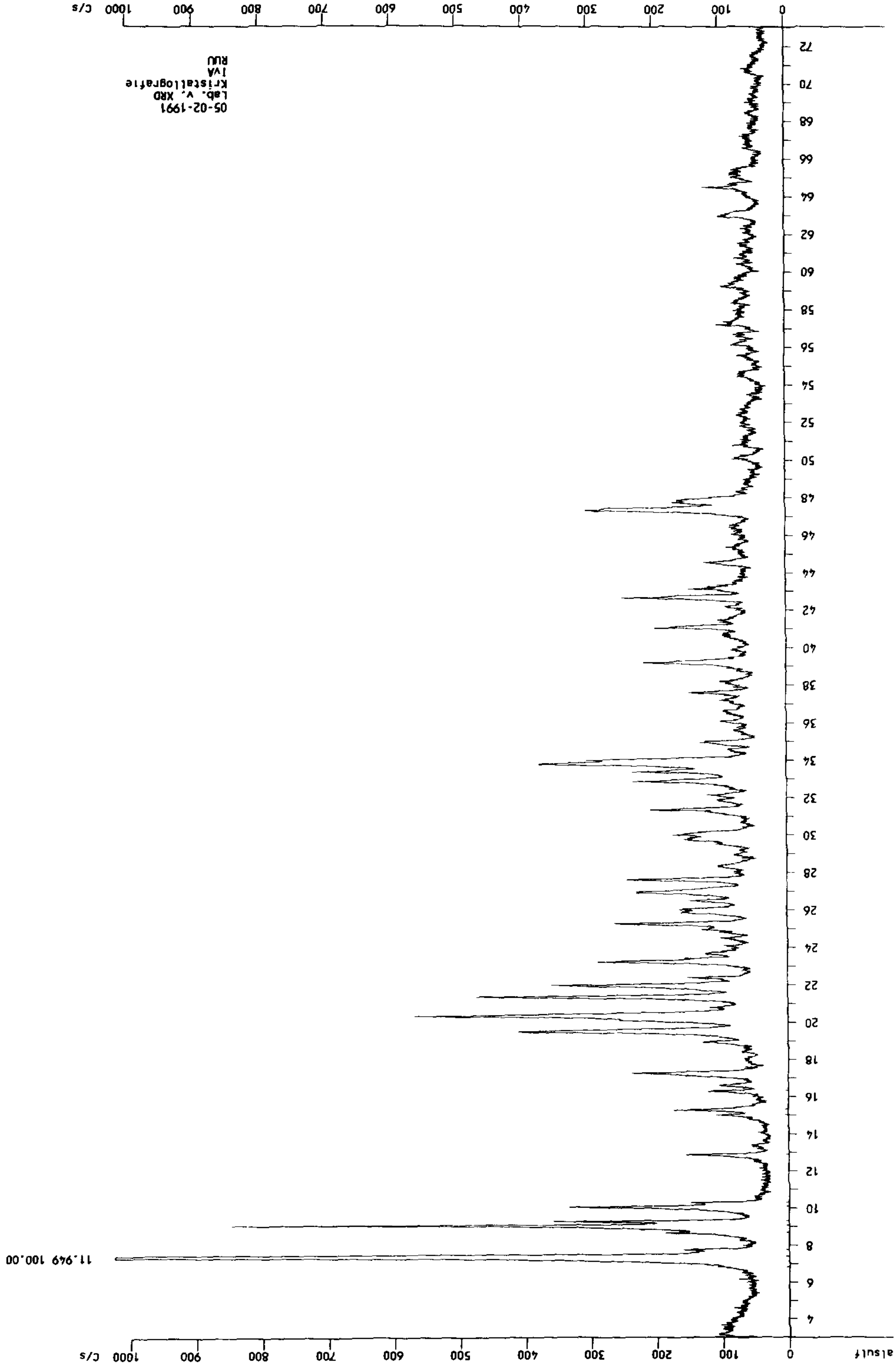


Fig. 2. X-ray powder diffraction pattern of the basic aluminum sulfate crystals.

TABLE 1

X-ray diffraction data in the range 3–50° 2θ of washed basic aluminum sulfate from the wall

d(obs)[a] (Å)	I (rel)	d(calc)[b] (Å)	hkl			d (Å)	
						[18]	[19]
12.07	100	12.18	002			12.3	12.2
11.49	8	11.50	010				
10.29	10	10.40	011			10.0	10.4
9.85	45	9.84	200			9.61	9.89
9.57	19	9.58	−111				
8.86	18	8.85	111			8.85	8.93
8.65	8	8.67	−202				
6.90	9	6.92	−212			6.83	6.53
5.89	6	5.94	212			5.83	
5.80	9	5.79	−204				
5.45	6	5.46	−121			5.37	5.33
5.34	5	5.32	311				
5.15	12	.5.15	−122			5.18	5.17
4.69	7	4.69	023				4.60
4.55	13	4.56	−412			4.58	
							4.47
4.37	30	4.37	214			4.37	4.36
4.27	6	4.28	−322				
4.16	25	4.15	321			4.17	4.10
4.05	18	4.05	−414				4.06
3.97	8	3.97	124				3.98
3.82	15	3.83	016			3.83	3.83
3.75	6	3.76	−422				3.65
3.57	6	3.57	511				
3.52	13	3.52	502			3.53	
3.44	8	3.46	−424			3.46	3.44
3.42	8	3.41	422				
3.36	8	3.36	−602	133		3.37	
3.30	13	3.30	324	330		3.33	3.33
3.23	13	3.23	−612			3.24	3.24
3.16	5	3.16	601			3.16	3.15
3.01	8	3.01	−118	504		3.00	3.02
2.97	9	2.97	−433			2.92	2.98
2.85	11	2.85	041			2.86	
2.81	5	2.81	−418			2.79	2.82
2.78	6	2.78	−711	036			
2.72	12	2.72	−714			2.73	
2.68	12	2.68	−328	531			2.69
2.65	19	2.65	604	−518	−341	2.65	
2.57	7	2.57	−419	−721	243	2.58	2.57
							2.50
2.39	8	2.39	−635			2.39	2.38
2.30	11	2.30	−718	−821	−731	2.30	2.32
2.20	11	2.20	−913	−912	−347	2.20	2.23
							2.18
2.12	12	2.12	617	445		2.12	
2.10	8	2.10	−831				2.10
2.03	6	2.03	−454			2.04	2.06
1.919	16	1.919	057			1.92	1.96
1.906	9	1.906	−10−23				

[a] Corrected d values shift 2θ, using Al as internal standard.

[b] Calculation based on: $a = 20.2$ Å; $b = 11.5$ Å; $c = 25.0$ Å; $\beta = 103°$; space group Pa or $P2/a$ [11].

resembles the patterns reported by Bersillon et al. [18] and Tsai and Hsu [20]. The basic aluminum sulfate exhibits a monoclinic unit cell (Fig. 2, Table 1). Aluminum was used as internal standard to correct systematic errors in the resulting 2θ values. Based on the unit cell parameters for the monoclinic basic aluminum sulfate [11], the pattern is indexed and unit cell parameters are recalculated using the first 38 reflections resulting in $a = 20.188 \pm 0.045$ Å, $b = 11.489 \pm 0.026$ Å, $c = 24.980 \pm 0.056$ Å and $\beta = 102.957 \pm 0.022°$ (Table 1).

The ^{27}Al MAS NMR spectrum of the unwashed precipitate from the bottom reveals one large 3650 Hz (at half height) broad Al(VI) resonance at 3.4 ppm (Fig. 1B). The crystals grown at the wall exhibit a large 3000 Hz broad Al(VI) resonance at 5.4 ppm and a small 500 Hz sharp Al(IV) resonance at 62.9 ppm. The resonances have a surface ratio Al(IV):Al(VI) of approximately 1:14 (accuracy 10–15%) (Fig. 1C). Washing of the wall crystals barely affects the ^{27}Al spectrum. The two signals at 63.0 ppm (700 Hz) and 5.7 ppm (2500 Hz) indicate a comparable surface ratio Al(IV):Al(VI) of approximately 1:13 (Fig. 1D).

The IR spectra of the unwashed precipitates from bottom and wall are comparable (Fig. 3, curves A and B) and exhibit typical absorption bands of OH at 3440, 1085 and 980 cm^{-1}, H_2O at 3247 and 1640 cm^{-1}, SO_4 at 1135, 980, 715, 610 and 566 cm^{-1} and NO_3 at 2425, 1787, 1085, 836 and 715 cm^{-1} (Table 2). Washing of the wall crystals results in the disappearance of the minor NO_3 absorption bands (Fig. 3, curve C).

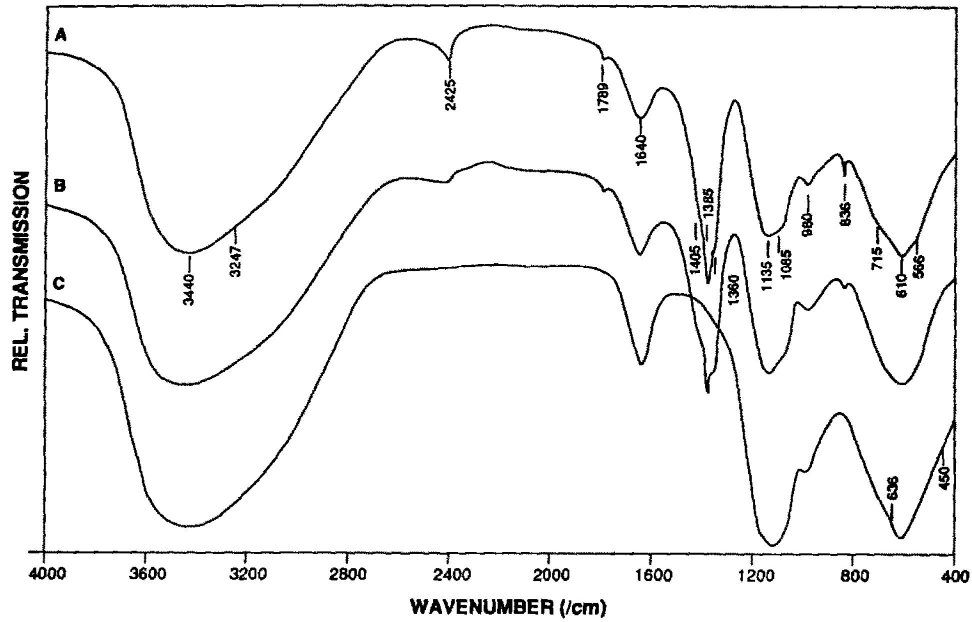


Fig. 3. IR spectra of (A) the unwashed crystals, (B) the precipitate on the bottom and (C) the washed crystals.

TABLE 2

IR absorption maxima (cm^{-1}) of the unwashed precipitate from the bottom and the washed crystals from the wall

Bottom (unwashed)	Wall (washed)		Assignment	
			Teargarden et al. [3]	Nyquist and Kagel [22], Gadsden [23]
3440 vs	3440	vs	3400 Al–OH stretch	Al–O–H stretch
3247 sh	3247			H–O–H stretch
2425 m				NO$_3$ $\nu_1 + \nu_3$ combination
1787 w				NO$_3$ $\nu_1 + \nu_4$ combination
1640 s	1640	s		H–O–H bending
1405 sh				NO$_3$ asym. stretch ν_3
1385 vs				NO$_3$ asym. stretch ν_3
1360 sh				NO$_3$ asym. stretch ν_3
1135 s	1135	vs		SO$_4$ stretch ν_3
1085 sh	1085	sh	1080 Al–OH bend	NO$_3$ Sym. stretch ν_1
980 m	980	s	970 Al–OH def. bend	SO$_4$ ν_1
836 m				NO$_3$ ν_2
			780 AlO$_4$ asym. stretch	
715 vw sh	715	sh		SO$_4$ + NO$_3$ ν_4
	636	w	640 AlO$_4$ sym. stretch	
610 s	610	s		SO$_4$ ν_4
566 sh	566	sh		SO$_4$ ν_2
	450	sh		SO$_4$ ν_2

Key: v, very; s, strong; m, medium; W, weak, sh, shoulder; sym., symmetric; asym., asymmetric.

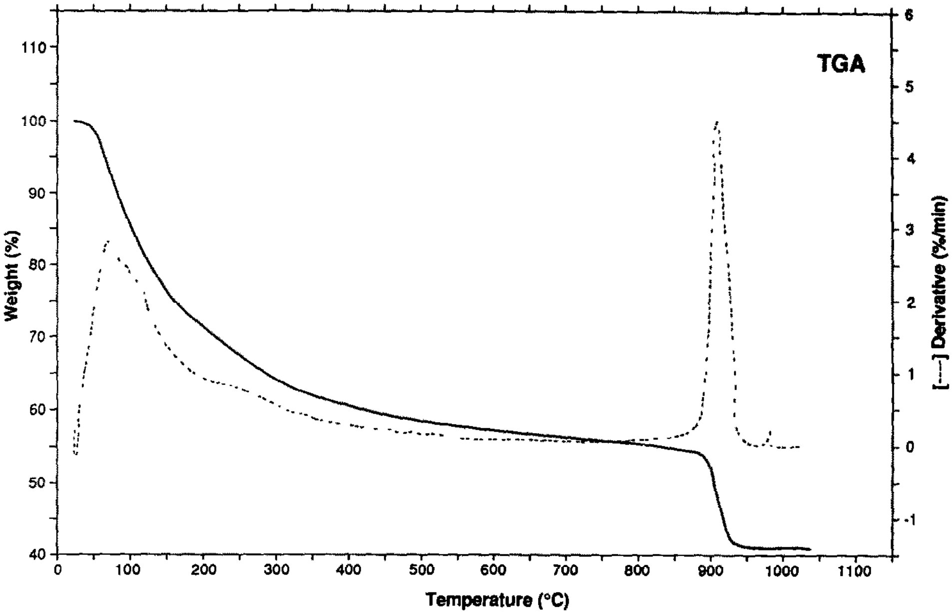
Thermal stability

Up to 80°C the HT-XRD pattern remains unchanged. Between 80 and 270°C a general decrease in d_{hkl} values is displayed, while the seven diffraction maxima between 5.5 and 4.2 Å merge into one faint band between 5.0 and 4.0 Å. Above 270°C all maxima disappear and the basic aluminum sulfate becomes X-ray amorphous.

TG analysis of the crystals exhibits four different steps of mass loss (Fig. 4(upper)). Between 25 and 80°C 10.5 mass% physically adsorbed water is lost. 28 mass% is lost in the range 80–360°C. A third mass loss of 6.5 mass% is recorded from 360 to 880°C. Finally, 12.5 mass% is lost between 880 and 950°C. The corresponding DTA profile (Fig. 4(lower)) shows major endothermic peak maxima at 120 and 930°C.

DISCUSSION

The ^{27}Al MAS NMR spectra have proven the presence of tetrahedral and octahedral positions in the tridecamer, which is a structural unit in the



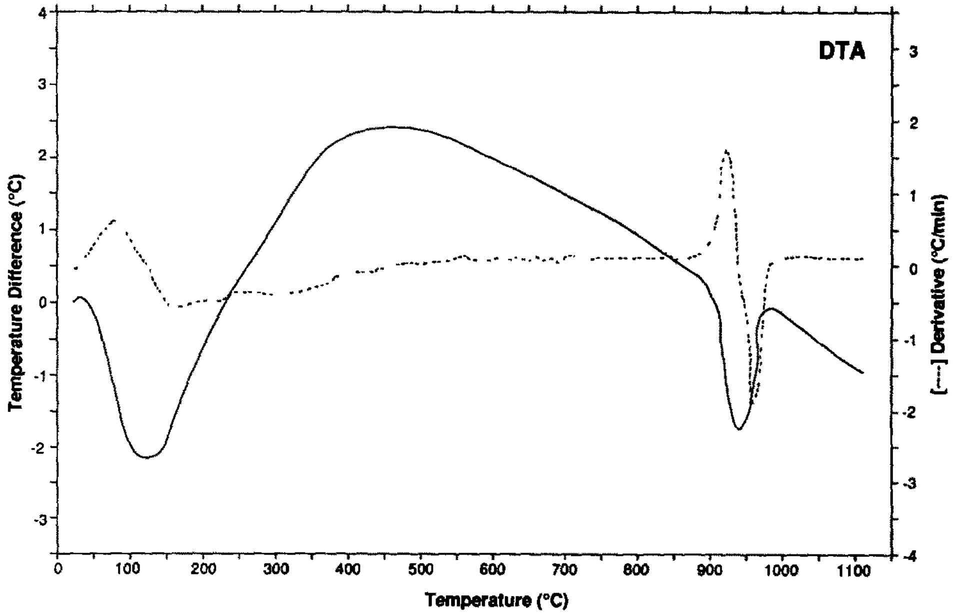


Fig. 4. (Upper) Thermogravimetric analysis and (Lower) differential thermal analysis of the basic aluminum sulfate crystals after washing.

TABLE 3

^{27}Al chemical shifts, δ (ppm) and full width at half height (FWHH) for Al(IV) and Al(VI)

	Al(VI)		Al(IV)		Al(IV):Al(VI)
	δ	FWHH	δ	FWHH	
$Na_{0.1}Al_{13}(SO_4)_{3.55}$ [a]	5.4	3000	62.9	500	1:14
$Na_{0.1}Al_{13}(SO_4)_{3.55}$ [b]	5.7	2500	63.0	700	1:13
$Al_{13}(SO_4)_3$ [d]		59			
$Al_{13}(SO_4)_4$ [c]	8 ± 5		62.8 ± 0.3	970	1:15
$Al_{13}(SO_4)_4$ [f]	3.6	3875	63.3		
$Al_{13}(SeO_4)_4$ [e]	8 ± 5		62.9 ± 0.3		
$Al_{13}Cl_6$ [c]			62.5		
$Al_{13}Cl_6$ [d]			62		
Zunyite [d,g]	0		69		
Zunyite [e,g]	8 ± 1		72.0 ± 1.0		

[a] This study, unwashed. [b] This study, washed. [c] [13]. [d] [14]. [e] [16]. [f] [15]. [g] Formula $[Al_{13}(OH, F)_{16}F_2]Si_5O_{20}Cl$.

crystals at the wall. The Al(IV):Al(VI) ratio of about 1:13 is very close to the theoretical ratio of 1:12 of the tridecamer. Previous investigations [13, 14] reported only the presence of tetrahedral resonances for the tridecameric sulfate and chloride. The absence of the octahedral resonances in these investigations was attributed to broadening due to the second order quadrupolar effects of the (1/2, −1/2) transition at lower magnetic field strength [16] and strong distortion of the aluminum octahedra [14] resulting in large quadrupole coupling constants [16]. Only zunyite $[Al_{13}(OH, F)_{16}F_2]Si_5O_{20}Cl$ gave a detectable octahedral signal (Table 3). Kunwar et al. [16] measured both octahedral and tetrahedral resonances at high magnetic field strength, but the Al(IV):Al(VI) ratio was not reported. Bottero et al. [15] calculated an Al(IV):Al(IV) ratio of 1:6.7, without correction for the overlap of both resonances and their spinning sidebands due to large variations in the quadrupolar coupling constants. After correction for this overlap an Al(IV):Al(VI) ratio of 1:16.4 was calculated [15].

The X-ray powder diffractograms reveal a monoclinic unit cell, which is in agreement with the chemical analysis of the washed, almost sodium-free crystals. The structural formula $(Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_{3.55} \cdot xH_2O)$ based on the ICP-AES data points to the presence of $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ units rather than those of $[Al_{13}O_4(OH)_{25}(H_2O)_{11}]^{6+}$ in the basic aluminum sulfate crystal structure, as was suggested by Müller et al. [13], Lampe et al. [14] and Schönherr et al. [21]. The calculated unit-cell parameters are almost identical to those for the sodium free basic aluminum sulfate with space group *P*2/*a* or *Pa*

[11]. The results of the ^{27}Al MAS NMR and of the IR spectra, which exhibit vibrations of Al–OH, Al–O_4 and H_2O comparable with those of basic aluminum chloride [3] and of the SO_4 groups, support the structure determined by Johansson [9, 11].

The 10.5 mass% loss of physically adsorbed water during heating from room temperature up to 80°C is equivalent to $x = 9$ in the formula: $Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_{3.55} \cdot xH_2O$, which agrees well with the 10–14 H_2O reported by Johansson [9]. This observation is comparable with that of Müller et al. [13] for basic aluminum chloride, which loses adsorbed water during a mild thermal treatment to 104°C. The HT-XRD results prove that this dehydration does not change the lattice of the basic aluminum sulfate. The loss of 28.5 mass% in the temperature range from 80 to 360°C is due to the disappearance of 12 mol of H_2O from the tridecameric unit and another 12 mol of H_2O from the neighboring 24 hydroxyl groups. Theoretically, based on the presence of the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ unit, these losses should represent two times 14 mass%, which agree well with the determined loss of 28.5 mass%. The HT-XRD results exhibit a decrease in d_{hkl} values in the temperature range from 80 to 270°C, due to the destruction of the basic aluminum sulfate structure, which ultimately results in X-ray amorphous material with a composition of $Na_{0.1}Al_{13}O_{16}(SO_4)_{3.55}$. The remaining mass loss must be caused by the disappearance of 3.55 mol of SO_3. This will produce a theoretical loss of 18.5 mass%, which is slightly lower than the observed loss of 19 mass%, leaving mainly aluminum oxide with a small amount of sodium oxide as final products. The observed thermal decomposition of the basic aluminum sulfate indicates that during calcination all water and hydroxyl groups are removed from the tridecameric polymer structure. This implies that at calcination temperatures higher than approximately 360°C the aluminum pillars in pillared clays convert into aluminum oxide.

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