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Communication

Synthesis of a lamellar calcium aluminate hydrate (AFm phase) containing benzenesulfonic acid ions

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Abstract

The formation conditions, crystallographic properties, and stability of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ at different temperatures and relative humidities were studied using X-ray powder diffraction, thermal and optical methods, and infrared spectroscopy. Further investigations in the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ at 23°C at 100 and 35% relative humidity were made. No solid solutions series $C_3A \cdot (1\text{-}x)Ca(C_6H_5SO_3)_2xCa(OH)_2 \cdot nH_2O$ $0 \leqslant x \leqslant 1$ were formed, either at 100 or 35% relative humidity. The lattice parameter of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35 and 100% were refined using least squares refinement with $a_0 = 0.5780 \pm 0.0001$ nm and $c_0 = 1.5784 \pm 0.0006$ nm at 100% relative humidity and $a_0 = 0.5763 \pm 0.0001$ nm and $c_0 = 1.5752 \pm 0.0002$ nm at 35% relative humidity.

Keywords: Hydration; Characterization; Organic acids; Monosulfate

1. Introduction

In cement chemistry, AFm phases such as $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $C_3A \cdot CaSO_4 \cdot 12H_2O$ [1–3] play an important role as hydration products of C_3A and C_4AF. The basic structure of AFm phases is made of sequences $[Ca_2Al(OH)_6]^+$ (mainlayer) and $[X \cdot nH_2O]^-$ (interlayer) perpendicular c_0. Calcium ions are sited in the octahedral cavities of the hexagonal $Al(OH)_6$ network [3]. Due to an additional coordination of an oxygen atom and a water molecule of the interlayer, the coordination number of the calcium atoms is seven [3,4]. In the interlayer, single or double charged anions of organic [5–7] or inorganic origin can be fixed.

$C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ was synthesised to study the influence of benzenesulfonic acid on the course of hydration of ordinary Portland cement and the in situ fixation of benzenesulfonic acid ions in the interlayer of lamellar AFm phases.

Therefore, investigations on the formation conditions and the stability concerning temperature and relative humidity of calcium aluminate benzenesulfonate hydrates were realised. Furthermore, the incorporation of large ions in relation to structural possibilities was determined in order to get results of the phase relations of lamellar calciumaluminatehydrates with organic ions. The investigations on the pure phase $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ can be used as a research model for further AFm phases containing sulfonic acid anions.

2. Methods

2.1. Synthesis of pure $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$

The preparation of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ was done using different raw materials of reagent grade quality. Fresh CaO was prepared by burning pure $CaCO_3$ at 1000°C for 3 h. $CaO \cdot Al_2O_3$ was prepared by burning molar amounts of CaO and γ-Al_2O_3 at 1350°C for 2 days. $3CaO \cdot Al_2O_3$ was burnt at 1400°C for 3 days with grinding in between. The calcium salt of the benzenesulfonic acid was prepared by addition of $CaCO_3$ to a benzenesulfonic acid solution and further evaporation at 40°C.

Pure phases of lamellar calcium aluminate benzenesulfonate hydrate were synthesised in three different ways. To investigate the stability of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ under extent of 2 mole $Ca(C_6H_5SO_3)_2$, the following reaction mixture was prepared as shown in Eq. (1)

$$\begin{aligned} &CA + 2CaO + 3Ca(C_6H_5SO_3)_2 \cdot H_2O + nH_2O \\ &\quad \rightarrow C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O \\ &\quad + 2Ca(OH)_2 + C_6H_5SO_3^- \end{aligned} \qquad (1)$$

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Reaction mixtures for investigations in the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ were prepared stochiometrically with $C_3A \cdot (1\text{-}x)Ca(C_6H_5SO_3)_2xCa(OH)_2 \cdot nH_2O$ $0 \leq n \leq 1$ in steps of $n = 0.1$.

The whole synthesis of the lamellar calciumaluminatebenzenesulfonatehydrate was performed under a CO_2-free atmosphere. A glove box with continuous circulation of N_2 was used to avoid carbonation that would cause the crystallisation of $C_3A \cdot 0.5Ca(OH)_2 \cdot 0.5CaCO_3 \cdot 11{,}5H_2O$ or $C_3A \cdot CaCO_3 \cdot 11{,}5H_2O$. The homogenised raw materials were placed in sealed polyethylene bottles and mixed with a water/solid ratio of 10 using CO_2-free water. The pastes were shaken continuously for 4 months to improve the formation of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$. The bottles were stored in a box filled with hydro-lime to prevent diffusion of atmospheric CO_2 into the bottles. The reaction temperature was kept constant at 23°C.

2.2. Investigation methods

Reactions 1 to 3 are shown in Eqs. (2), (3), and (4):

$$CA + 2CaO + Ca(C_6H_5SO_3)_2 \cdot H_2O + nH_2O \rightarrow C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O \quad (2)$$

$$CA + 3CaO + 2C_6H_6SO_3H + nH_2O \rightarrow C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O \quad (3)$$

$$C_3A + Ca(C_6H_5SO_3)_2 + nH_2O \rightarrow C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O \quad (4)$$

The precipitates of these reactions were filtered in a glove box and immediately investigated by X-ray powder diffraction. Si (99.999%) was used as an internal standard material. X-ray patterns of wet pastes were obtained at 100% relative humidity (rh) on a Siemens D5000 diffractometer with a special humidity camera of Paar Austria. Nitrogen at 100% rh was pumped through the climate camera to guarantee homogenous moist and CO_2-free conditions during the measurements. The samples were dried for further X-ray investigations in a box under circulating CO_2-free air at a rh of 35% using saturated $CaCl_2$ solution.

Scanning electron microscopy (SEM) techniques were used to get informations on particle size, habitus, and surface properties of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ crystals formed in reactions 1 to 3. Semiquantitative analysis were performed using the electron diffraction X-ray analysis (EDX) system. Chemical analysis was carried out using atomic absorption spectroscopy (AAS) to determine the CaO and Al_2O_3 concentrations. C and S amounts were analysed quantitatively by direct element analysis. The amount of water was determined by Karl-Fischer method and thermal analysis. The bonding energy of water molecules, stability ranges of different hydration stages of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$, and thermal stability of the benzenesulfonic ion were

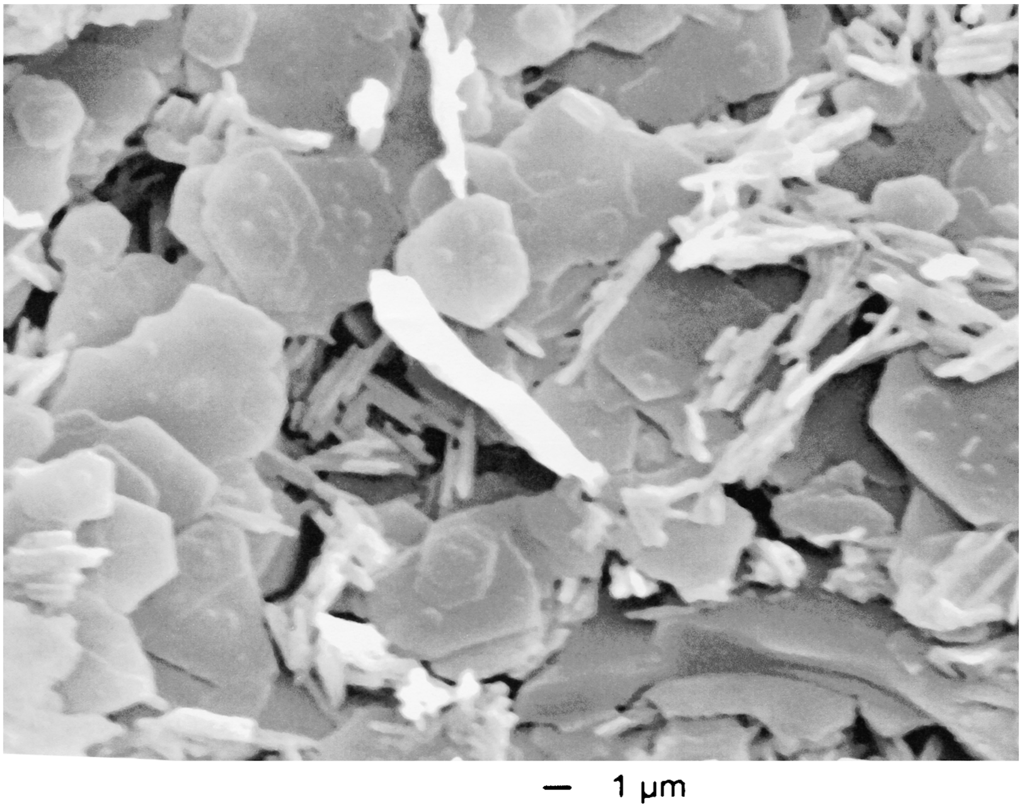

Fig. 1. SEM image of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$.

Table 1
Metric parameters of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ at 100% rh

a_o (nm)	c_o (nm)	γ (°)
0.5780 ± 0.0001	1.5784 ± 0.0006	120

Table 2
Chemical analysis of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh

Compounds	Measured weight (%)	Theoretical weight (%)
CaO	26.8	26.1
Al_2O_3	11.8	11.9
$(C_6H_5SO_3^-)$	36.5	36.7
H_2O	25.6	25.3
Total	100.7	100

Table 3
Metric parameters of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh

a_o (nm)	c_o (nm)	γ (°)
0.5780 ± 0.0001	1.5784 ± 0.0006	120

carried out by thermal analysis. Infrared (IR) spectroscopy was used to determine benzenesulfonic acid ions on the basis of the different IR vibrations of the SO_3H and C_6H_5 group. IR spectroscopy is also used to control CO_2 exclusion because minor contamination can be detected.

3. Results

After the reaction time of 4 months at a measured pH value of 12 to 13, the precipitates were investigated immediately by X-ray powder diffraction at 100% rh. The lamellar phase $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ crystallised even under excess of extra 2 mole $Ca(C_6H_5SO_3)_2$. No ettringite-like phase could be detected by X-ray diffraction methods. Due to the typical platy hexagonal habit (Fig. 1), a preferred orientation of the crystals in the sample holder occurred. Therefore the intensities of (00l) reflections in powder patterns are extremely high. The hexagonal unit cell with the dimensions a_o and c_o (Table 1) contains one layer with the composition of $[Ca_2Al(OH)_6]^+ \cdot [C_6H_5SO_3 \cdot nH_2O]^-$.

The reflections were indexed and refined on the basis of a hexagonal cell with the following specifications: after drying $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ to 35% rh over a saturated $CaCl_2$ solution, the composition $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ (Table 2) was calculated on the basis of the chemical analysis. The metric parameters refined on the basis of reflections of powder patterns measured at 35% rh show a small decrease of 0.004 nm in c_o (Table 3).

Using thermal analysis and Karl-Fischer methods, lower hydrates were determined at higher temperatures. Two overlapping endothermic processes with an onset temperature at 45 and 80°C were determined using differential scanning calorimetry (DSC) (Fig. 2). According to the weight loss curve (Fig. 3), two steps were detected (Table 4). The first step at 45°C is due to the loss of six molecules or H_2O

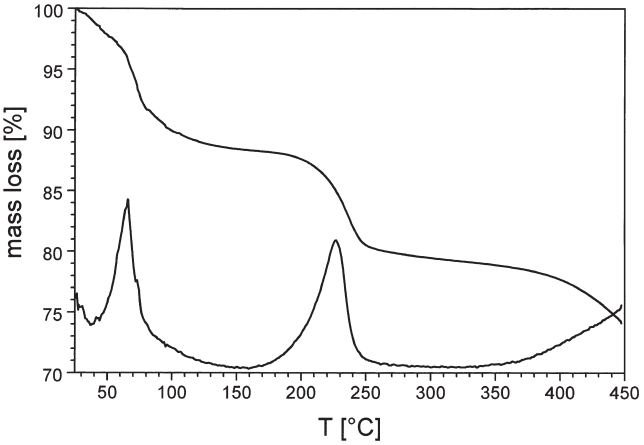

Fig. 3. Thermal analysis TG/DTG of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh.

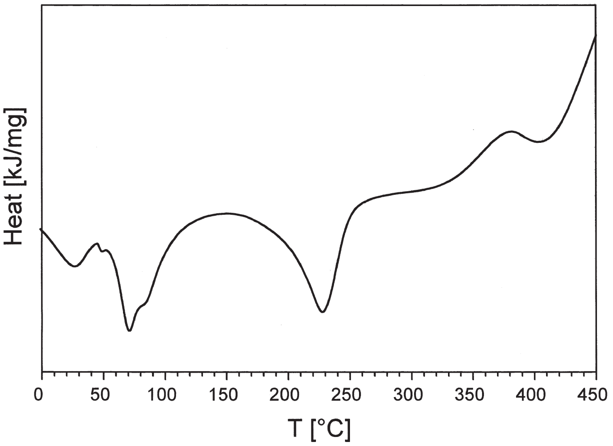

Fig. 2. DSC of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh.

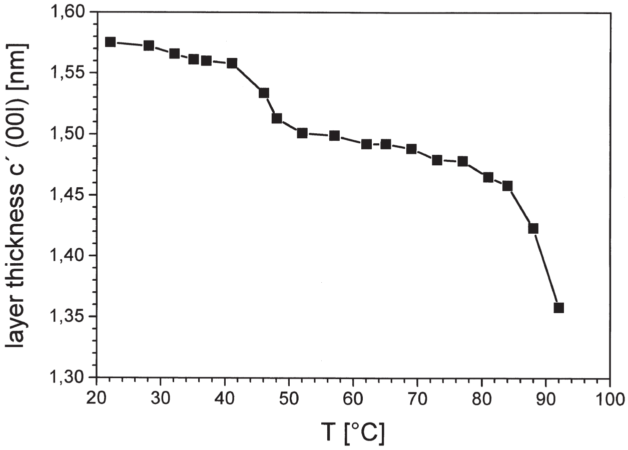

Fig. 4. Decrease of the interlayer dimension c' of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh with increasing temperature.

Table 4
Dehydration of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh

	Temperature (°C)	Weight loss (%) N_2 atmosphere	H_2O (mole)
$[(C_6H_5SO_3)_2 \cdot 6H_2O]^{2-}$	RT	0	12
	45	11.7	6
$[Ca_2Al(OH)_6]^{2+}$	200	20.6	3

Table 5
Development of the layer thickness c' of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at different temperatures

Temperature (°C)	H_2O	c' (nm) = $d_{(001)}$	Chemical composition of the interlayer
25	6	1.575	$[(C_6H_5SO_3)_2 \cdot 6H_2O]^{2-}$
40	0	1.558	$[(C_6H_5SO_3)_2 \cdot 0H_2O]^{2-}$
$\sim$80	0	$<$1.358	X-ray amorphous

Table 6
IR frequencies of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$

Wave number (cm^{-1})	Vibration type
3650	OH vibration of the mainlayer
3560	$\nu_1(H_2O)$
3460	$\nu_3(H_2O)$
3050	ν (C-H)
1630–1620	ν (C=C) and ν_2 (H_2O)
1485	ν (C=C)
1450	ν (C=C)
1310	ν (S=O)?
1200–1170	Sulfonic ion
1125	ν (S=O)
1065, 1045	δ (C-H) and ν (SO_3)
1020, 1000, 850–840	δ (C-H)
755	δ (C-H)
690	δ (C-C)
670	ν (C-S)
635	Sulfonic ion
560	Al-O vibrations
550	Metal-OH vibrations
425, 300–310	Ca-O vibrations

of the interlayer $[(C_6H_5SO_3)_2 \cdot 6H_2O]^{2-}$ at 35% rh. The second step at 200°C describes the release of three molecules of structurally necessary H_2O of the mainlayer $[Ca_2Al(OH)_6]^{2+}$. Further dehydration reactions of the mainlayer could not be determined because of the destruction of the organic compound. In combination with high temperature X-ray diffraction (XRD) (Fig. 4) the layer distances c' (Table 5) decreases with increasing temperatures and the layer distance c' reduces to 1.558 nm.

The fixation of benzenesulfonic ions can be detected qualitatively using IR spectroscopy (Fig. 5, Table 6). C-C single (690 cm^{-1}) and double bondings (1630–1620, 1480, and 1450 cm^{-1}) of the aromatic ring system and the S-O bondings (1200–1170 cm^{-1} and 1125 cm^{-1}) of the sulfonate group indicate the fixation of the organic anion in the interlayer of the salt structure. Carbonation effects [8] could not be detected. Further absorption lines [see Eqs. (2) through (4)] in the region of 3600 cm^{-1} indicate water molecules fixed in the interlayer of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh and OH vibration of the mainlayer. At lower wave numbers the absorption lines of Al-O and Ca-O bondings are visible.

In the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ (Fig. 6), the stable phases under equilibrium are $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$ and $C_3A \cdot Ca(OH)_2 \cdot 18H_2O$ and under 35% rh are $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ and $C_3A \cdot Ca(OH)_2 \cdot 12H_2O$. No intermediate phase or solid solutions were formed at either 100 or 35% rh. The amount of lamellar phases formed under equal conditions depends on the mixtures $C_3A \cdot (1\text{-}x)Ca(C_6H_5SO_3)_2xCa(OH)_2 \cdot nH_2O$ $0 \leqslant n \leqslant 1$. Amorphous gel phases were possibly formed at benzenesulfonic acid ion concentrations higher than 70 mole%

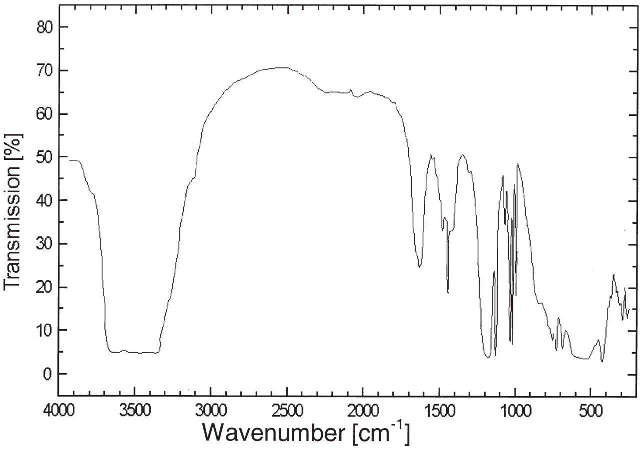

Fig. 5. IR spectra of $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 12H_2O$ at 35% rh.

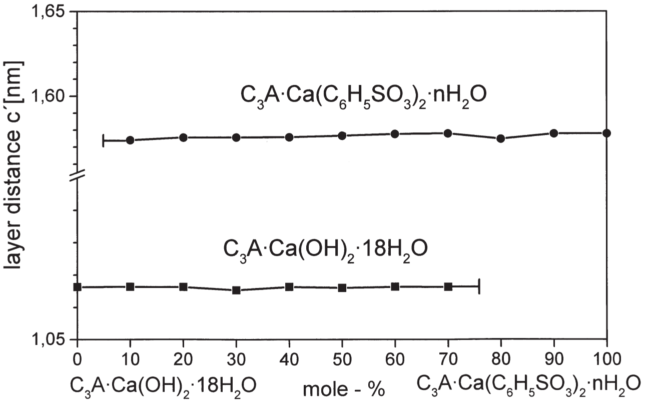

Fig. 6. Layer distance c' in the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot 18H_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ at 100% rh.

in the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ at 100% rh [5].

4. Discussion

It could be proved that benzenesulfonic acid anions can be fixed in the interlayer of lamellar calciumaluminatehydrate. Neither solid solution series nor intermediate phases were formed in the system $C_3A \cdot Ca(C_6H_5SO_3)_2 \cdot nH_2O$-$C_3A \cdot Ca(OH)_2 \cdot nH_2O$ at 100 and 35% rh. $[Ca_2Al(OH)_6]^+ \cdot [C_6H_5SO_3 \cdot nH_2O]^-$ and $[Ca_2Al(OH)_6]^+ \cdot [OH \cdot nH_2O]^-$ were the only hydration products. Higher $C_6H_5SO_3^-$ concentrations led to the formation of gel structures. No phases with ettringite-like structures crystallised. The metric parameters of the unit cell of calciumbenzenesulfonatehydrate were refined by least squares methods of X-ray patterns taken at 100 and 35% rh with layer distances at 1.5784 ± 0.0006 and 1.5752 ± 0.0002 nm, respectively. The hydrates at 100 and 35% rh crystallise hexagonally.

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