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Synthesis and characterisation of sulfite-containing AFm phases in the system $CaO\text{-}Al_2O_3\text{-}SO_2\text{-}H_2O$

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Abstract

The use of sulfite-containing waste materials mainly from flue gas desulfurization causes the formation of new lamellar phases (AFm) in the field of calcium aluminum hydrates. The incorporation of sulfite anions in the structure of lamellar calcium aluminate hydroxy salts and solid solutions with tetracalcium aluminate hydrate will be shown. Using special synthesis conditions a sulfite containing ettringite (AFt) was synthesized. Besides the pure synthesis of phases, the thermal stability, the hydration stages, and other properties of sulfite-containing phases were investigated. Solid solutions of lamellar calcium aluminate hydroxy salts are discussed.

Keywords: Waste management; Ettringite; Hydration; Hydration products; X-ray diffraction

Sulfite-containing waste materials may result from flue gas desulfurization processes. Fluidized bed ashes or residues from semidry flue gas purification systems contain sulfur oxides in different oxidation stages, depending on the oxidation conditions in the cleaning process and the humidity of the atmosphere [1–3]. Besides the sulfur compounds, these waste materials contain ashes with pozzolanic activity, nonhydraulic material, not reacted sorption chemicals such as calcium hydroxide and calcium carbonate, but also reaction compounds such as chlorides and fluorides.

The possibility of use of calcium sulfite to control the setting and hardening of ordinary portland cement (OPC) was studied by others [4–6]. They described a setting behaviour quite similar to those OPCs with calcium sulfate addition [7,8] and investigated the hardening process of fly ashes in the presence of calcium sulfite and calcium hydroxide. Calcium sulfite shows a positive effect on the strength development in the presence of $Ca(OH)_2$ compared to mortars with calcium sulfate. Other authors described a decrease in the compressive strength of sulfite containing mortars [4].The composition of calcium sulfite-containing hydration products are of interest in order to investigate the course of hydration of hydraulic materials in the presence of sulfite anions. Different calcium sulfite containing hydrates are described in the literature [9–18]. Tables 1 and 2 summarize chemical and crystallographic data of the known hydrates.

For an application of sulfite-containing products in building material industry, a better understanding of the hydration reactions and of the properties of the sulfite-containing hydrates is necessary.

1. Methods

1.1. Synthesis

For the synthesis of calcium sulfite-containing hydrates of the aluminate phase pure $CaSO_3 \cdot 1/2H_2O$ was synthesized by pumping SO_2 gas into a calcium hydroxide solution, causing precipitation of calcium sulfite hemihydrate (Hannebachite). The end of the reaction was controlled by pH measurement. Filtering and drying of the precipitates was done in a glove box under nitrogen atmosphere. Completely dried $CaSO_3 \cdot 1/2H_2O$ is stable against oxidation in air. Calcium sulfite hemihydrate was used to study the hydration reaction of calcium aluminate in the presence of sulfite ions. The course of hydration was investigated by interference microscopy, heat flow calorimetry, and time dependent powder X-ray techniques.

The synthesis of calcium sulfite-containing hydration products (AFm phases) of the aluminate phase was performed using molar mixtures of CA (burnt from CaO and γ-Al_2O_3 at 1400°C), CaO (decarbonated $CaCO_3$ at 1000°C), and Na_2SO_3. Different molar ratios were used according to

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Table 1
Crystallographic data of calcium sulfite containing hydrates (d_{001} for AFm phases)

Formula	d_{001} (Å)	Reference
$C_3A \cdot CaSO_3 \cdot 7H_2O$	8.51	[15]
$C_3A \cdot CaSO_3 \cdot 11H_2O$	8.57	[22]
$C_3A \cdot CaSO_3 \cdot 11H_2O$	8.55	[23]
$C_3A \cdot CaSO_3 \cdot 12H_2O$	8.489	[18]
$C_3A \cdot CaSO_3 \cdot 11H_2O$	8.54	[5]
$C_3A \cdot 2/6CaSO_3 \cdot 4/6Ca(OH)_2 \cdot 11H_2O$	8.40	[16]
$C_3A \cdot 2/6CaSO_3 \cdot 4/6CaCO_3 \cdot 11H_2O$	7.82	[16]
$C_3A \cdot 3CaSO_3 \cdot 32H_2O$	–	[16]

Table 2
Chemical compositions of sulfite-containing calcium aluminum hydrates (pure compounds and solid solutions)

Trivial name	Chemical composition
Monosulfite	$3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$
Solid solutions of	$3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$
Monosulfite-monohydroxide	$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$
Sulfite ettringite	$3CaO \cdot Al_2O_3 \cdot 3CaSO_3 \cdot 32H_2O$

Table 3
Chemical analysis of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$

Content (mass%)	Measured	Theoretical
Na_2O	0.3	–
CaO	37.9	38.1
Al_2O_3	16.6	17.3
SO_2	11.1	10.9
H_2O	33.8	33.7

Table 4
Crystallographic data of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ (35% RH, 25°C)

Crystal system	Rhombohedral
Space group	P3, $P\bar{3}$
Lattice parameters	$a_o = 5.7709 \pm 0.0004$ Å $c_o = 51.284 \pm 0.005$ Å

Table 5
d_{001} values of the dehydration stages of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$

Temperature (°C)	Mole H_2O per formula	d_{001} (Å)
20	11	8.55
45	10	8.22
85	9	7.80
110	8	7.70
135	6	6.80

the following formula: $3CaO \cdot Al_2O_3 \cdot (1\text{-}x)CaSO_3 \cdot (x)Ca(OH)_2 \cdot 11H_2O$ ($0 < x < 1$). The homogenized mixtures were placed in polyethylene bottles, suspended with water (water/solid ratio approximately 40 ml/49 =10) and shaken for 6 months in order to get equilibrium synthesis. To avoid contamination with oxygen and CO_2 from air, all preparation and handling was done under nitrogen atmosphere in a glove box. Sulfite ettringite only could be synthesized using the saccharate method [16].

1.2. Investigation methods

X-ray diffraction was performed on wet samples under 100% relative humidity and on dry samples under 35% relative humidity in order to study different hydration stages in dependence of the humidity. Additionally the dehydration of the hydrates with increasing temperature up to 300°C was investigated using a special X-ray heating equipment.

Chemical analysis was done by Atomic Absorption Spectrometry (CaO, Al_2O_3, Na_2O), Photometry (sulfite detection as $BaSO_4$ after oxidation with H_2O_2), Karl Fischer titration (Metrohm), and thermogravimetry for H_2O-measurement (Seiko).

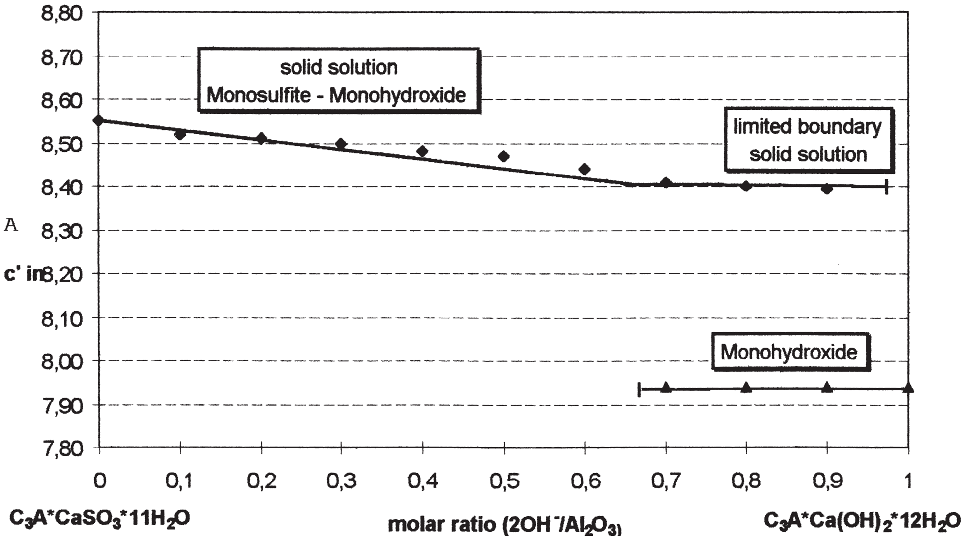

Fig. 1. System monosulfite-monohydroxide ($C_3A \cdot CaSO_3 \cdot 11H_2O$-$C_3A \cdot Ca(OH)_2 \cdot 12H_2O$) at 35% RH.

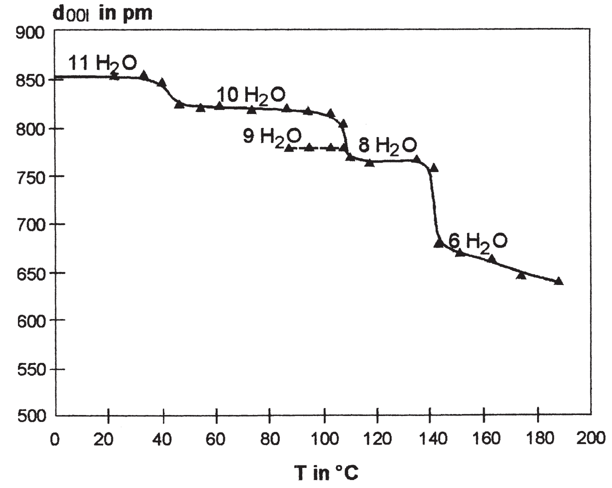

Fig. 2. Variation of d_{001} for different dehydration stages of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

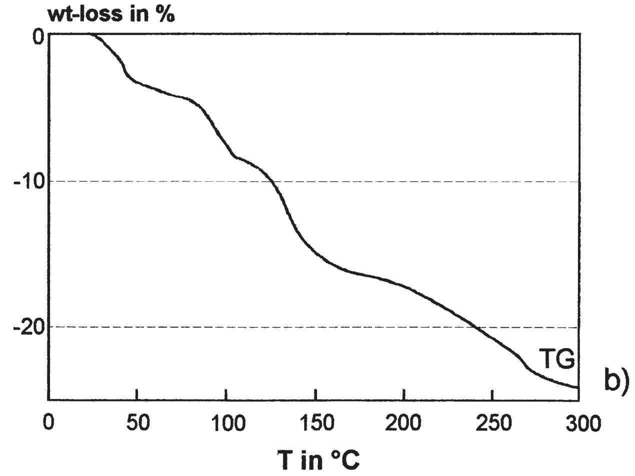

Fig. 4. TGA diagram of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ (detail of room temperature to 300°C).

The calcium sulfite-containing hydrates were additionally characterized by scanning electron microscopy, thermal analysis (thermogravimetry and differential scanning calorimetry) and by infrared spectrometry (IR) (Bruker).

2. Results

The precipitates from the bottle synthesis were filtered in a glove box and the wet paste was immediately studied by X-ray diffraction (XRD) in a climate-controlled chamber at 100% relative humidity. Afterward the paste was dried very softly in a CO_2-free atmosphere at 35% relative humidity (RH) and again studied by XRD. There is no dependence of the humidity in the basal peaks for the solid solutions, which indicate the thickness of the layer in the crystallographic *c* dimension. Tetracalcium aluminate hydrate, which coexists with a boundary solid solution as given in Fig. 1, dehydrates from C_4AH_{19} (100% RH) to C_4AH_{13} (35% RH). The water content of monosulfite can be determined definitely by 11 H_2O per formula at room temperature and 35% RH The X-ray data are given in the Appendix.

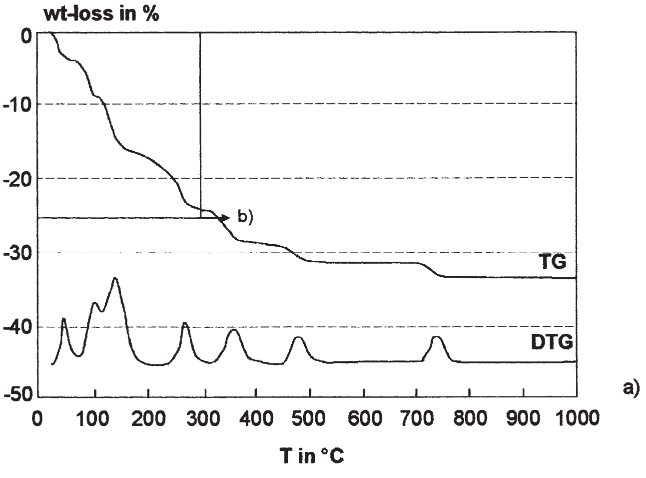

Fig. 3. TGA diagram of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

2.1. System $C_3A \cdot CaSO_3 \cdot 11H_2O$-$C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ (monosulfite-monohydroxide)

In the system $C_3A \cdot CaSO_3 \cdot 11H_2O$-$C_3A \cdot Ca(OH)_2 \cdot 12H_2O$ (monosulfite-monohydroxide), solid solutions occur in the range $C_3A \cdot (1\text{-}x)CaSO_3 \cdot (x)\ Ca(OH)_2 \cdot 11H_2O$ ($0 < x < 0.66$). At higher contents of hydroxide two phases coexist in the system. Tetracalcium aluminate hydrate coexists with a solid solution $C_3A \cdot (0.34)CaSO_3 \cdot (0.66)\ Ca(OH)_2 \cdot 11H_2O$. The pure compound $C_3A \cdot CaSO_3 \cdot 11H_2O$ (monosulfite) was synthesized and the properties determined under definite conditions.

2.2. Investigation of $C_3A \cdot CaSO_3 \cdot 11H_2O$ (monosulfite)

The pure compound $C_3A \cdot CaSO_3 \cdot 11H_2O$ was investigated in detail using different methods for analysis.

The overall chemical composition that was determined from these syntheses is summarized in Table 3. The crystal-

Table 6
Water stages determined for $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ by TG analysis

Temperature (°C)	Mass loss (m%)	Rest of water
20	–	11 H_2O
40	2.6	10 H_2O
100	8.9	8 H_2O
120	16.2	6 H_2O
260	24.4	Dehydration of the main layer
350	28.5	
480	31.0	
740	32.2	

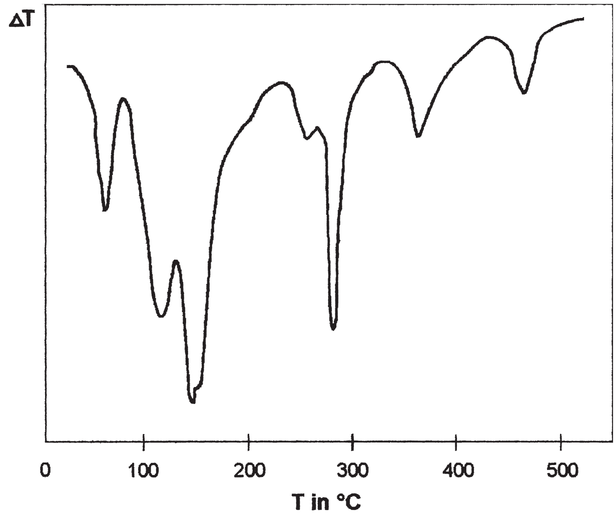

Fig. 5. DSC diagram of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

lographic data of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ (monosulfite) were determined using structural basic data according to monosulfate [19]. The least squares refinement of the powder diffraction data results are given in Table 4.

On heating monosulfite, a dehydration of the interlayer occurs and different hydration stages can be clearly differentiated from each other by measuring the basal spacing in *c* direction (see Table 5). The corresponding water content was quantified by thermogravimetry and Karl Fischer titration.

The pure synthesized monosulfite was analyzed by thermogravimetry methods and by differential scanning calorimetry in order to investigate the behaviour of monosulfite at elevated temperatures, to study the dehydration schemata,

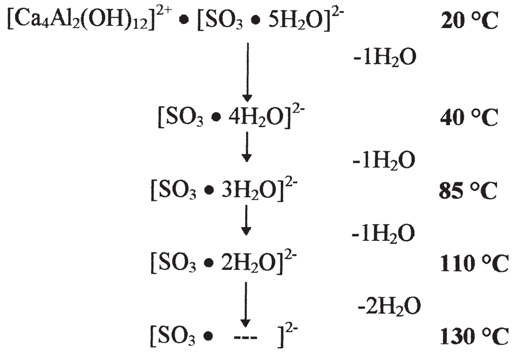

Fig. 6. Dehydration schemata for $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

and to determine the water contents (Fig. 2). Fig. 3 shows the thermogravimetric analysis (TGA) diagram of monosulfite and Fig. 4 shows the corresponding dehydration part from 25 to 300°C, indicating the dehydration of the main layer. The dehydration of the main layer is followed by the loss of structural necessary water and the breakdown of the structure begins at temperatures above 260°C (Table 6). In the DSC diagram the dehydration of monosulfite up to 260°C and the following deterioration of the main layer is shown in Fig. 5.

Summarizing all the results from thermoanalyses and high temperature X-ray measurements, a dehydration scheme for monosulfite $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ can be established according Fig. 6.

The SEM investigation shows the typical platy, hexagonal shape of the monosulfite (Fig. 7). The crystal shape is very similar to other lamellar phases in the whole group of

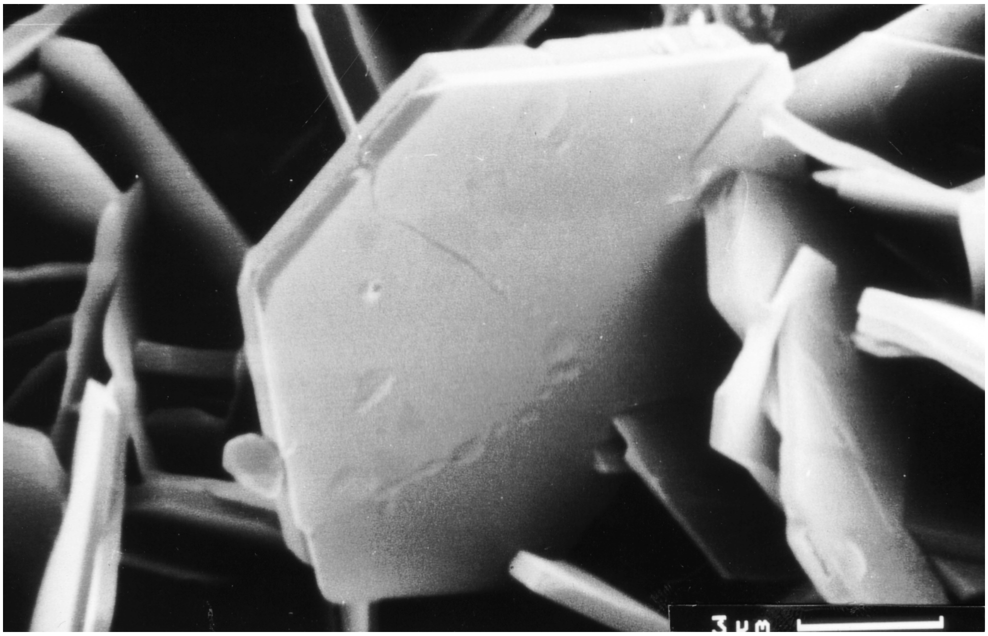

Fig. 7. SEM micrograph of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

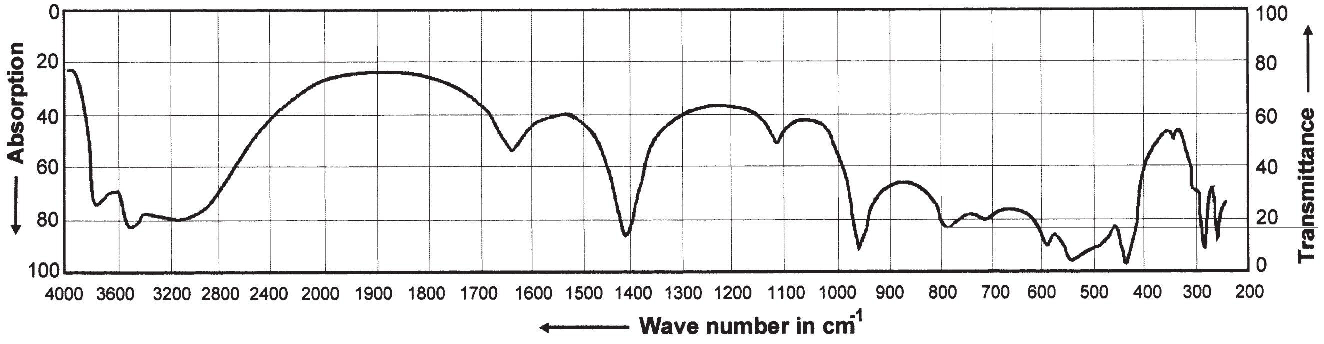

Fig. 8. IR spectrum of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$.

AFm phases. It is not possible to distinguish between monosulfate and monosulfite by means of SEM investigations.

The presence of sulfite instead of sulfate can be demonstrated clearly using spectroscopic methods. The IR diagram of monosulfite is given in Fig. 8. The corresponding interpretation by the table of vibrations is summarized in Table 7. Despite very careful preparation a small amount of sulfate can be already distinguished in the IR diagram. The method therefore can be used to determine small amounts of sulfate and to document the stage of oxidation occurring in the sample.

2.3. *Investigation of $3CaO \cdot Al_2O_3 \cdot 3\ CaSO_3 \cdot 32H_2O$ (sulfite ettringite)*

A calcium aluminate hydroxy salt with ettringite structure was synthesized according the procedure described previously [20] using the saccharate method. The properties of this phase were described earlier [16,17,20]. The X-ray powder data are given by (ICDD)-JCPDS-number 41-217 (International Centre for Diffraction Data, Swarthmore, PA, USA). Under the conditions of paste reaction no synthesis of an ettringite-type mineral containing sulfite was possible. At high sulfite concentrations a new phase was detected. The chemical composition and the properties still need to be determined, but it does not belong to an ettringite-like compound.

Table 7
Vibrations in the IR spectrum of $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$

Wave number (cm^{-1})	Vibration
280	
•	
•	Ca-O vibration
420	
480	
•	Al-O vibration
•	Me-OH vibration
960	
1105	ν_3–SO_4^{2-} vibration
1405	ν_3–SO_3^{2-} vibration
1645	ν_2-H_2O deformation vibration
3000	
•	valence vibration of
•	the interlayer water
3600	
3650	OH vibration of the
3670	main layer

3. Comparison of hydration reactions

The initial hydration reactions of aluminate with sulfate forms an ettringite compound. The initial hydration product with sulfite is a lamellar phase (AFm). Due to the chemical compositions besides the pure $3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_2O$ (monosulfite), solid solutions with OH and CO_3^{2-} can also occur. A corresponding lamellar iron-containing phase with the composition $3CaO \cdot Fe_2O_3 \cdot CaSO_3 \cdot 12H_2O$ was previously described [21].

By oxidation of sulfite to sulfate, solid solutions of the lamellar phases occur. Depending on the concentrations of the anions phase assemblages of lamellar sulfite containing phases with sulfate-ettringite can also occur. Therefore we have to control for the precise identification and determination of the phases several parameters simultaneously in the investigation steps (pH value, concentrations, oxidation, carbonisation, temperature, relative humidity, and solid so-

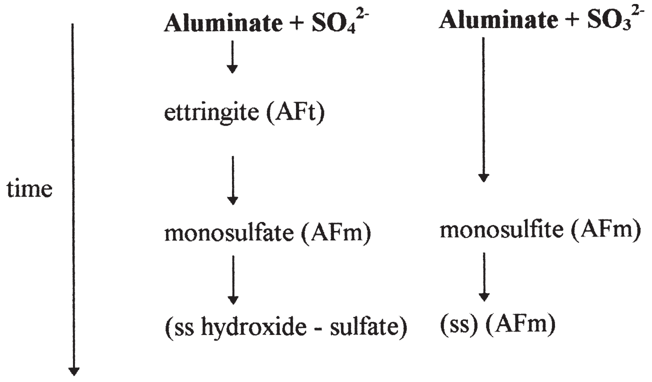

Fig. 9. Reaction schemata for aluminate with sulfate and sulfite (ss = solid solution).

lutions). A reaction schemata for sulfate and sulfite is given in Fig. 9.

4. Discussion

The hydration of the aluminate phase of cements in the presence of sulfite leads to the formation of lamellar phases (AFm) containing sulfite. At all concentrations investigated no sulfite ettringite was stable. Sulfite ettringite (AFt) only crystallized under the conditions of saccharate method. From calorimetric data it could be shown that the silicate phase is slightly accelerated by sulfite ions. In the presence of sulfate and sulfite it is highly probable that complete solid solutions of the lamellar phases exist. In addition, the oxidation the carbonation of the lamellar phase does not lead to the formation of ettringite, but to ternary solid solutions of the composition $3CaO \cdot Al_2O_3 \cdot (x)\ CaSO_3 \cdot (y)\ CaCO_3 \cdot (z)\ Ca(OH)_2 \cdot nH_2O$ (with $x + y + z = 1$). The oxidation of lamellar calcium aluminum salts containing sulfite to sulfate seems to be very slow. In the next steps the reactions of the aluminate phase under the combined influence of carbonate, sulfate, chloride, hydroxide, and sulfite will also be shown. Investigations for the description of the hydration reactions are in progress.

Acknowledgments

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Appendix

X-ray powder data of monosulfite ($3CaO \cdot Al_2O_3 \cdot CaSO_3 \cdot 11H_20$)

2Θ	I/Io	*d* values (Å)	*h*	*k*	*i*	*l*	Δ 2Θ
10.34	100	8.548	0	0	0	6	−0.001
20.77	80	4.273	0	0	0	12	+0.003
22.54	45	3.941	1	0	−1	8	+0.001
24.88	3	3.576	1	0	−1	10	+0.025
30.96	35	2.886	1	1	−2	0	−0.005
31.40	1	2.847	0	0	0	18	+0.030
32.22	1	2.776	1	1	−2	5	+0.021
32.73	10	2.734	1	1	−2	6	+0.001
33.16	5	2.699	1	0	−1	16	−0.016
34.70	3	2.583	1	0	−1	17	−0.003
34.83	10	2.574	1	1	−2	9	+0.010
35.65	5	2.516	1	1	−2	10	−0.022
36.08	1	2.487	2	0	−2	2	−0.002
36.61	30	2.453	2	0	−2	4	+0.004
37.59	20	2.391	1	1	−2	12	+0.011
38.65	10	2.328	2	0	−2	8	+0.011
39.32	3	2.289	2	0	−2	9	−0.017
39.47	15	2.281	1	0	−1	20	+0.007
39.71	3	2.268	1	1	−1	14	−0.021
40.12	5	2.246	2	0	−2	10	+0.015
40.90	5	2.205	1	1	−2	15	+0.010
40.97	2	2.201	2	0	−2	11	+0.029
42.27	2	2.136	0	0	0	24	+0.012
42.77	15	2.112	1	0	−1	22	+0.004
43.34	1	2.086	1	1	−2	17	−0.016
43.84	3	2.063	2	0	−2	14	+0.023
44.67	15	2.027	1	1	−2	18	+0.011
46.00	3	1.971	1	1	−2	19	−0.004
46.03	3	1.970	2	0	−2	16	+0.016
46.17	1	1.965	1	0	−1	24	+0.008
48.47	1	1.877	2	1	−3	3	+0.030
48.68	2	1.869	2	1	−3	4	−0.002
48.97	1	1.859	2	1	−3	5	−0.021
49.63	5	1.835	1	0	−1	26	−0.016
49.78	3	1.830	2	1	−3	7	−0.028
50.98	15	1.790	2	0	−2	20	−0.006
51.52	1	1.772	2	1	−3	10	+0.008
53.33	2	1.716	1	1	−2	24	+0.029
53.56	2	1.710	0	0	0	30	−0.002
53.70	1	1.705	2	0	−2	22	−0.028
54.64	1	1.678	2	1	−3	14	+0.226
55.07	20	1.666	3	0	−3	0	−0.009
56.20	5	1.635	3	0	−3	6	−0.006
56.53	2	1.627	2	1	−3	16	+0.032
59.49	5	1.553	3	0	−3	12	−0.014
59.65	5	1.549	2	0	−2	26	−0.019
60.24	1	1.535	3	0	−3	13	−0.011
60.62	2	1.526	1	0	−1	32	−0.006
60.85	5	1.521	2	1	−3	20	−0.007

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