Characterization of Different Water Contents of Ettringite and Kuzelite

H. Pöllmann
Martin-Luther University of Halle/Saale
Germany

Abstract

Aft and AFm-phases are well known compounds in cement chemistry. Due to temperature, relative humidity and composition the water content can vary.
The water bounding capacity of the hydrated materials is influenced by this stochiometry of different water contents of phases. The compounds were synthesized in the laboratory and investigated by X-ray diffraction, chemical methods, thermogravimetry SEM and Karl-Fischer titration. The following different phases were identified :

C_3A $CaSO_4.nH_2O$ with 16/14/12/11/10.5/9- water molecules

C_3A $3CaSO_4.nH_2O$ with (32+x)/ 32/30/26 – water molecules

The different water contents are due to different excess water contents not necessary for the cristalline structure. These water molecules can be incorporated additionally in the interlayer (Afm-phases) or in the channels of the Ettringite-structure.
By careful measurements the different phases can be distinguished.

1. Introduction

Ettringite and lamellar calcium aluminium hydroxi salts are well known in cement chemistry and due to their variable composition and wide solid solution often described as Aft and Afm-phases. Also their stability and occurrence in cementitious materials is summarized[1,3,6,7,8, 10, 11-22, 25-27, 32, 36-40, 42, 49, 54-59, 61, 62, 64-66, 69-77].
Crystal structure determinations were performed by [2, 4, 5, 9, 43, 44, 68].

2. Methods

The different calcium aluminium hydroxi salts were synthesized as pure phases under exclusion of CO_2 in a glove box. Reagent grade chemicals were used for all synthesis work. The chemical compositions were determined by ICP-OES (Ca, Al), Ion-chromatography (Sulphate) and Karl-Fischer-titration (water contents). Loss of ignition and water loss at definite temperatures was also obtained using thermoanalytical measurements. Carbonate absence was proofed by IR-spectroscopy.. The drying of Ettringite and Kuzelite at definite relative humidities was established by pumping CO_2-free air through concentrated salt solutions. Lower hydration stages of phases were also obtained at elevated temperatures and studied by X-ray measurements data at elevated temperatures using Panalytical X-Pert and Bruker D5000 diffractometers equipped with special high temperatures cells (PAAR) and X´celerator or scintillation detectors. Hydration reactions of calcium aluminates with calcium sulfate were followed by heat flow calorimetry. The sensitive hydrates were also characterized using special Kryo-transfer electron microscopy.

3.Results

The synthesis of phases were performed using the coprecipitation method at water/solid ratios between 10 and 25. Reaction equations using stochiometric calculations and tricalciumaluminate are given in equation 1. Aluminiumsulphate hydrate , Calcium sulfate hydrates, CaO made from freshly calcined $CaCO_3$, (Merck, Fluka), decarbonized water) were used in stochiometric proportions at a water to solid ratio between 10 (Afm-phases) and 25 (Aft-phases) and reaction times of 7 days to 3 month.
The mixtures were shaken continuously in polyethylene bottles and filtrated and prepared under exclusion of CO_2 in a glove box.
Investigations were performed beginning from a wet slurry by X-ray diffraction using special humidity cells. The X-ray patterns were indexed and the lattice parameters refined. Using existing crystal structures the corresponding theoretical X-ray diagrams were calculated using the program Powdercell. The comparison of da ta with existing JCPDS data and new measurements proofed different problems in interpretation.

3.1. Ettringite

Calculations to synthesize pure ettringite are given in equation 1. No excess of additional ions is given:

Ettringite :

$$\mathbf{C_3A + 3CaSO_4 + nH_2O \dashrightarrow 3CaO.Al_2O_3.3CaSO_4.(32+n)H_2O}$$

Monosulfate(Kuzelite):

$$\mathbf{3CaO.Al_2O_3.3CaSO_4.(32+n)H_2O+2C_3A+nH_2O \dashrightarrow 3CaO.Al_2O_3.CaSO_4.(12+n)H_2O}$$

Equation 1 : Reactions of C_3A to form Ettringite and Kuzelite

Relevant reactions using aluminum sulfate are given in equation 2 :

$$\mathbf{Al_2(SO_4)_3 + 6CaO + nH_2O \dashrightarrow 3CaO.Al_2O_3.3CaSO_4.(32+n)H_2O}$$

Equation 2 : Coprecipitation method to form ettringite and ongoing Kuzelite

The determination of the lattice parameters of these synthesized ettringites shows a decrease with falling relative humidity .and increasing temperature excluding any solid solution.
Figure 1 shows part of the X-ray diagram of pure sulfate-ettringite in comparison to the existing JCPDS-files of ettringite with the same given chemical composition of pure Sulfate-ettringite. It is obvious that some differences occur and an explanation of these differences could be found by the different water contents of the new formed phases.

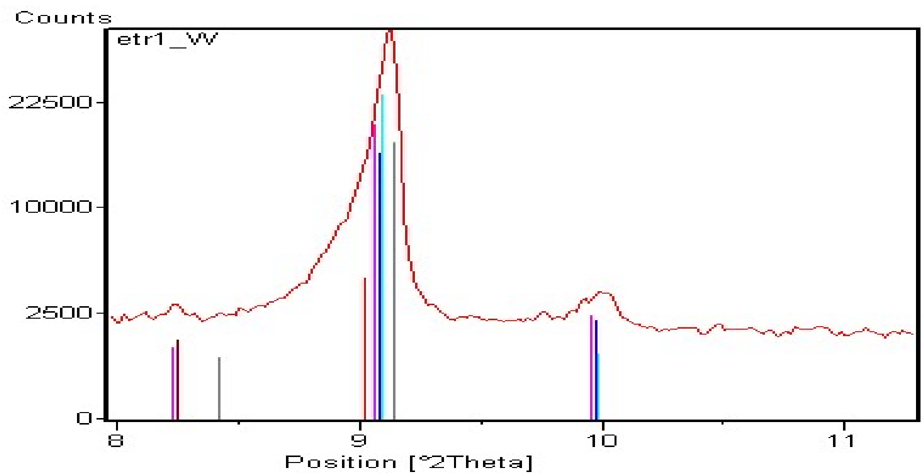


Fig. 1 : Part of an X-ray diagram (8-11 degree 2-theta) of pure sulfate-ettringite in comparison to 3 relevant JCPDS-data of pure sulfate ettringites

In figure 2 the results of the syntheses of pure sulfate ettringites at definite r.h. and temperatures are shown. The water contents of these phases were additionally determined by TG and KF-titration.

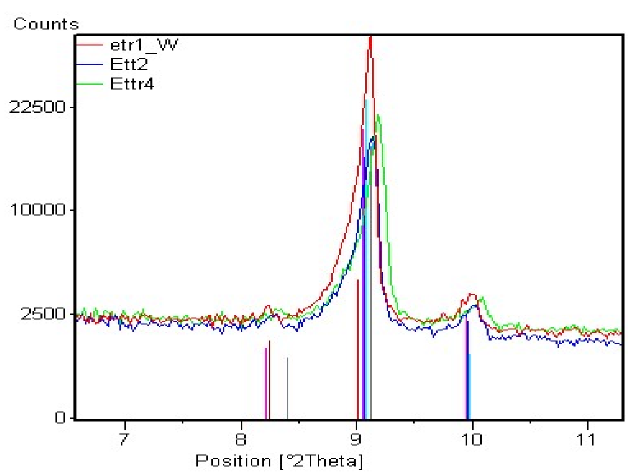


Fig. 2 : Different X-ray diagrams of pure synthesized sulfate-ettringites at different measurement conditions a) 100 % r.h. b)dried, c) dried

using acetone

The corresponding lattice parameters are given in table 1.

$[Ca_6Al_2(OH)_{12} . 24H_2O]$ $[(SO_4)_3 . 6H_2O]$ 100 % r.F.

V = 2367 $Å^3$ a_o = 11.26 Å, c_o = 21.56 Å

$[Ca_6Al_2(OH)_{12} . 24H_2O]$ $[(SO_4)_3 .2H_2O]$ 35 % r.F.

V = 2342 $Å^3$ a_o = 11.22 Å, c_o = 21.48 Å

$[Ca_6Al_2(OH)_{12} . 24H_2O]$ $[(SO_4)_3. 0H_2O]$ Acetone-dried

V = 2289 $Å^3$ a_o = 11.14 Å, c_o = 21.30 Å

Tab 1: Lattice parameters of ettringites with different water contents

In pure systems it is possible to determine the precise water content and the lattice parameters quite exactly. Figure 3 shows the differences in total loss of ignition when solid solution with OH-ettringite or carbonate ettringite occur on a theoretical basis. It is obvious that no difference in the determination between 10 mole % of solid solution with OH-ettringite and a varying water content of pure sulfate ettringite can be established.

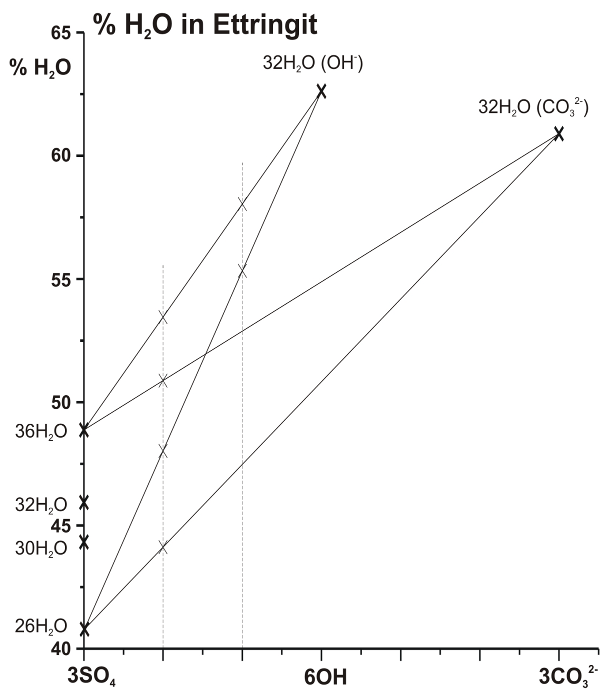


Fig. 3 : Comparison of water contents of pure sulphate-, carbonate-, and hydroxide-ettringite. The water contents were varied between 26 and 36 molecules of water. Intersection lines show theoretical lines of relevant solid solutions between these ettringites

3.2 Kuzelite

After the synthesis of pure Kuzelites the monophased precipitates were characterized by in-situ X-ray investigations at definite r.h. and temperatures and the corresponding water contents were determined by TG and KF-titration. The relevant water stages and conditions are given in table 2. Figure 4 shows a comparison of the X-ray diagrams of different water stages of Kuzelite. It is obvious that the (00l)-reflections clearly can be separated for the different phases.

•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 10H_2O]^{2-}$	
		< 100 % r.F.
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 8\ H_2O]^{2-}$	
		25°C
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 6H_2O]^{2-}$	
•		45°C
$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 5H_2O]^{2-}$	
•		55°C
$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 4.5H_2O]^{2-}$	
•		80 °C
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 3H_2O]^{2-}$	
•		170°C
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4]^{2-}$	

Tab. 2 : Hydration stages of Kuzelite at different relative humidities and elevated temperatures

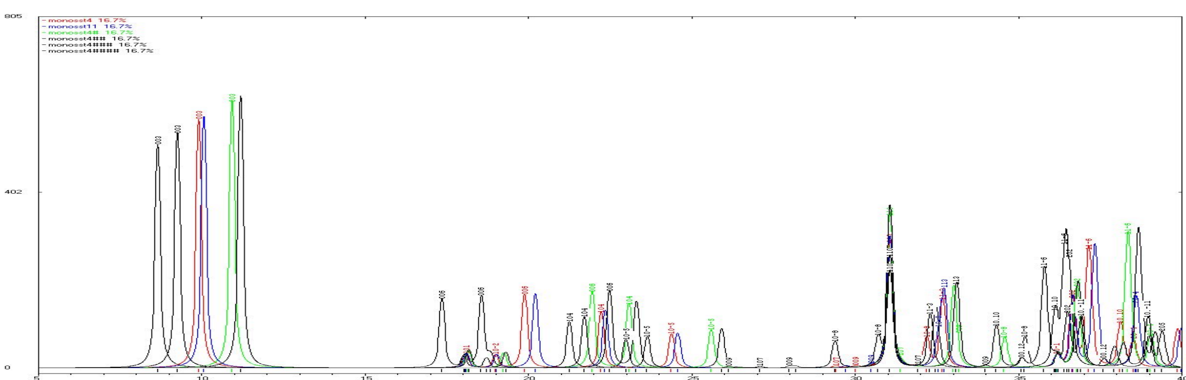


Fig 4: Theoretical X-ray diagrams of different hydration stages of Kuzelite showing shift of (00l)-peaks and constant place of (hk0)-indices

The following lattice parameters for monosulfate could be established and are given in table 3 :

Chemical composition		Lattice parameters(Å) a_o	c_o	JCPDS-No.
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 10H_2O]^{2-}$	5.7	30.67	44-602
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 8\ H_2O]^{2-}$	5.748	28.69	42-0062
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 6H_2O]^{2-}$	5.76	26.79	45-158
$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 5H_2O]^{2-}$		~26.4	-------
$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 4.5H_2O]^{2-}$		~ 24.3	-------
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4 \cdot 3H_2O]^{2-}$		~ 23.7	-------
•$[Ca_4Al_2(OH)_{12}]^{2+}$	$[SO_4]^{2-}$			-------

Tab. 3 : Lattice parameters of hydration stages of Kuzelite (Monosulfate) obtained from ICPDS-No.s and own measurements.

4.Summary and Discussion

The synthesis of pure phases of Sulfate-ettringite and pure Kuzelite and the determination of the properties of these phases clearly shows that 3 different hydration stages of ettringite and 6 different hydration stages of Kuzelite occur due to varying relative humidity and temperature. The water bonding capacity of both minerals is summarized in table 4 :

Water bonding capacity of Ettringite and Kuzelite :

Ettringite – (AFt)		Kuzelite (AFm)	
36 H_2O	48.9 %	16 H_2O	41.5 %
32 H_2O	44.3 %	12 H_2O	34.0 %

Tab. 4 : Water bonding capacity of Ettringite and Kuzelite

The complex solid solution also influences the properties and it must be clearly pointed out that often only a combination of methods provides enough exact data to establish definite compositions of both minerals. It is obvious that the incorporation of iron into sulfate-ettringite leads to a compensation of the decrease of lattice parameter c_o in carbonate and hydroxide-rich solid solution. Always chemical measurements are necessary for correct interpretation of lattice parameter changes.

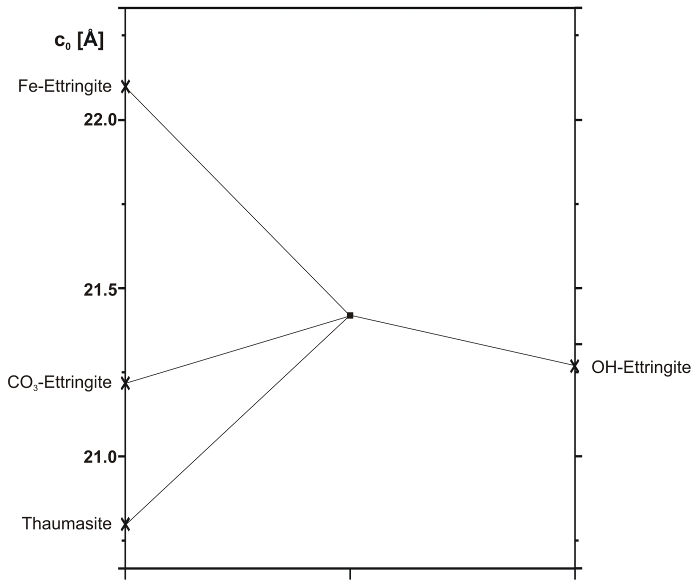
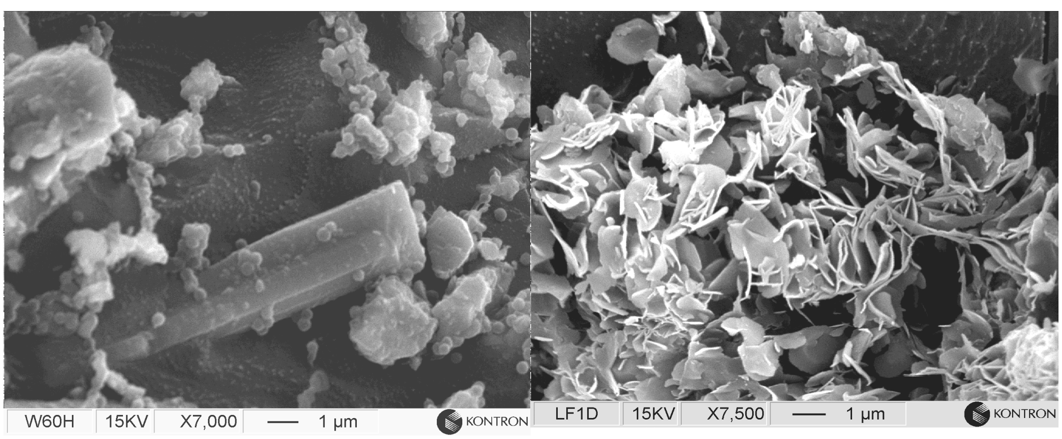


Fig. 5 : Lattice parameter c_o of Sulfate-ettringite in comparison to Carbonate-ettringite, Hydroxide-ettringite and Fe-Sulfate-ettringite

The overall interpretation of data needs, besides the varying water contents, also the characterization of solid solutions with carbonate and hydroxide and silicon- and iron-incorporation in Ettringite. SEM-images of unaffected phases can be obtained by Kryo.SEM only (figure 6).



a) b)

Fig 6 a,b: Kryo-SEM images of a) Ettringite and b) Kuzelite showing no dehydration effects

5. Acknowledgement

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6. References

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