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Cr^{6+}-containing phases in the system $CaO-Al_2O_3-CrO_4{}^{2-}-H_2O$ at 23 °C

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ABSTRACT

Synthesis and investigation of lamellar calcium aluminium hydroxy salts was performed to study the incorporation of chromate ions in the interlayer of lamellar calcium aluminium hydroxy salts. Different AFm-phases (calcium aluminate hydrate with alumina, ferric oxide, mono-anion phase) containing chromate were synthesized. These AFm-phases belong to the group of layered double hydroxides (LDHs).

$3CaO\cdot Al_2O_3\cdot CaCrO_4\cdot nH_2O$ and $C_3A\cdot 1/2Ca(OH)_2\cdot 1/2CaCrO_4\cdot 12H_2O$ were obtained as pure phases and their different distinct interlayer water contents and properties determined. Solid solution of chromate-containing phases and tetracalcium-aluminate-hydrate (TCAH) were studied. The uptake of chromate into TCAH from solutions was proven. Chromate contents in solution decrease to <0.2 mg/l.

1. Introduction

Chromium in cement and the reaction behaviour was studied in [1–6]. Chromate and its incorporation in ettringite and lamellar calcium aluminium hydroxy salts is a long known effect and can help to reduce toxic Cr^{6+} in solution. The use in immobilization was described in [7–20]. Nevertheless until present, mainly chromate fixation in ettringite is described in detail in [21–24]. The incorporation of chromate in AFm-phases, solid solutions, water contents and relevant properties are only poorly understood, despite many observations on the interlayer incorporation are mentioned. Also the use in environmental applications for removal of chromate is described in literature [25–28]. Detailed results on definite crystallizing phases are not available yet. Incorporation in LDH's was studied in [29–38]. General aspects of LDH's and incorporation of cations and anions are given in [40–43]. This paper describes the different AFm-phases based on the cations calcium and aluminium and containing chromium in the 6± state. The properties and solid solution series with TCAH of these phases were studied. Chromium also can be incorporated in AFm-phases to replace aluminium in a trivalent stage [22,42]. For chromate containing phases also their yellow colour can be used as an additional simple, but fast indication.

2. Synthesis

The synthesis of AFm-phases was performed using paste reaction with starting materials monocalcium aluminate (synthesized applying laboratory reaction of $CaCO_3$ and γ-Al_2O_3 at 1350 °C, with intermediate grinding, the fraction $<60\ \mu m$ was used for following hydration reaction, calcium oxide (synthesized by decarbonization reaction of $CaCO_3$ at 1000 °C for 1 h) and $CaCrO_4$ (synthesized by reaction of solutions of CrO_3 and CaO, followed by precipitation of calcium chromate, adding methanol. The precipitated $CaCrO_4$ was dried carefully at 400 °C to establish definite composition.

The paste reactions were performed using stochiometric portions of CA (monocalcium aluminate) CaO and $CaCrO_4$ in polyethylene bottles and CO_2-free freshly distilled water with w/s ratios of 5–10. The preparation procedure was performed in nitrogen atmosphere inside a glove box to avoid carbonisation reactions of the AFm-phases.

All handling of the samples, starting with the synthesis, filtration, drying and preparation of samples for further investigation was performed in N_2-atmosphere in a glove box to avoid contamination by CO_2.

X-ray investigation of the humid samples were carried out using a special X-ray sample holder which could be filled in the glove box with nitrogen to avoid carbonisation. X-ray investigations of the dried samples were made using a special tool of back-loading to avoid strongly textured samples, Si ($a_o=5.4308$ Å, MERCK) was added as an inner standard. X-ray diffractometers of Bruker D 5000 and Panalytical equipped with X'celerator detector and special humidity and high temperature cells were applied. The lattice parameters were determined by indexing and least squares refinement of humid and dried samples. The different hydration stages of the Chromate-AFm-phases were determined by in-situ high temperature X-ray diffraction (Anton Paar high temperature cell, HTK 16) and thermal analysis using thermogravimetry and DSC-techniques with a SEIKO-instrument(TG/DTA 320, DSC 120/220). Water contents were established by Karl-Fischer titration. SEM-investigations were carried out using a

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JEOL-instrument (JSM 6300). IR-investigations were performed using pressed KBr-pellet techniques in a Bruker spectrometer. The anion exchange reactions of OH and chromate were performed in chromate-containing water suspensions of TCAH with different ratios by shaking in polyethylene bottles for different times and following filtration to separate solids and solutions. Chemical analyses were performed using ICP-OES (ZEISS Jena Plasmaquant 110) and ICP-MS (Thermo-instruments PQ Excell). Chromate contents were determined using a UV–VIS spectral photometer (CADAS 100).

3. Results

3.1. Synthesis and characterization of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$

3.1.1. Background

In 1949 already, AFm-phases with tetragonal coordinated anions were mentioned in [42] using a synthesis method of precipitation from Na-aluminate and alkali chromate solutions. [43] synthesized a compound with the composition $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$, even as single crystals up to 1 cm in diameter. The dehydration behaviour of this compound $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ was already described as very complex dehydration reactions with different hydration stages of the interlayers were not solved completely, due to very narrow temperature ranges of the various lower hydrates [43].

3.1.2. Methods

Synthesis of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ was performed using stochiometric proportions of CA, CaO, and $CaCrO_4$ and Portlandite-satured solutions (w/s-ratio=10) at 25 °C and reaction times between 3 months and 12 months. The paste reaction was applied by continuous movement of the polyethylene bottles using a shaking unit. The achieved size of the Chromate–AFm-crystals was in the range of 2–10 μm. The bottles with the different mixtures were filtrated after completion of the reaction time in a glove box and investigated by powder diffractometry at 100% r.h. using a special humidity chamber. The different relative humidities were established by pumping nitrogen through saturated salt solutions and through the AFm-phases powders until a definite water stage of the interlayer of the phases was obtained. After drying the samples to 35% r.h. the samples were investigated by X-ray diffractometry again. The different dehydration stages were determined using DSC, TG-measurements, performed on samples dried to 35% r.h., followed by high temperature X-ray diffraction to get the X-ray data of the different hydration stages. A chemical analysis of the dried sample is summarized in Table 1, establishing an overall water content at 35% r.h. of 12 mol per formula unit.

A DSC-diagram of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ is given in Appendix A1.

The dehydration of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ starts already at 35 °C, followed by different other dehydration steps. 6 different lower dehydration stages were determined (Table 2). At 250 °C, the main layer of the AFm-phase also starts to dehydrate and the compound becomes X-ray amorphous. At temperatures exceeding 255 °C also the influence of Cr^{6+}-reduction to Cr^{3+} can be seen, when thermoanalytical measurements are performed in inert gas atmosphere. The TG-curve of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ is shown in Fig. 1 showing the different lower hydration stages of monochromate.

After destruction of the AFm-lattice the initial different hydration stages of the AFm-phases are followed at higher temperatures by newly formed reaction compounds like $C_{12}A_7$ ($12CaO–7Al_2O_3$ or mayenite) $CaCrO_4$, CaO, $Ca_5[(OH)/(CrO_4)_3]$ (apatite structure with different chromium valencies) and $3CaO \cdot 3Al_2O_3 \cdot CaCrO_4$ in different amounts.

Table 1
Chemical composition of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ (35% rel. humidity, 25 °C).

Oxide	Weight % theor.	Weight % (measured)
CaO	34.9	35.1
Al_2O_3	15.9	15.7
CrO_3[a]	15.5	15.3
H_2O	33.7	33.9
$\sum$	100	100

[a] CrO_3 recalculated from chromate determination.

Table 2
Water stages of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ and stability ranges.

T (°C)	Water content of compound	$d_{(001)}$ (Å)
25	12	9.74
30–34	~11?	9.15
30–34	~10?	8.75
35	9	8.40
95	8	8.10
155	6	6.75

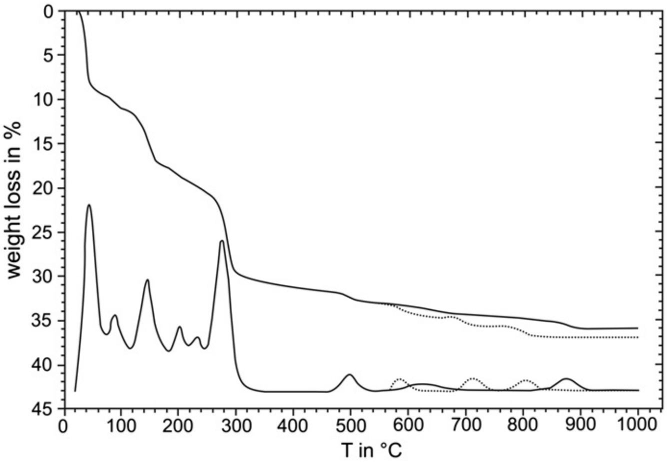


Fig. 1. TG-curve of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$.

The different hydration stages of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ at temperatures up to 200 °C can be described by the $d_{(001)}$-values given in fig. 2 (d-values of hydration stages measured by high temperature X-ray diffraction and relevant data are summarized in Table 2). The different dehydration stages can easily be followed by measuring the relevant (00l)-reflections of layer structures.

The phase is composed of a positively charged main layer $Ca_4[Al_2(OH)_{12}]^{2+}$ and a negatively charged interlayer $[CrO_4 \cdot nH_2O]^{2-}$ containing the anion and different amounts of additional water. The amount of water depends on temperature, type of anion and relative humidity.

Table 2 shows the hydration stages, d-values of (00l)-reflections and the temperatures of hydration stages. Water contents of 11 and 10 water molecules only can be assumed, because they can be identified by a shift of X-ray peaks in a narrow temperature region and only at 35 °C a phase containing 9 water molecules, can be clearly separated. This phase is stable over an

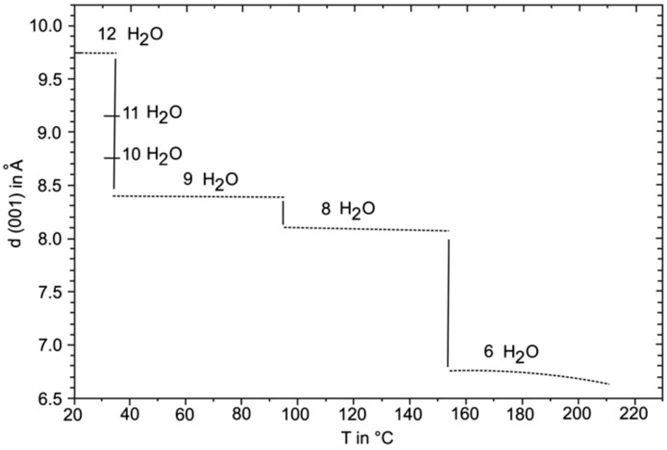


Fig. 2. $d_{(00l)}$-values of different hydration stages of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ measured by high temperature X-ray diffraction. ($n=12H_2O$, $11H_2O$, $10H_2O$, $9H_2O$, $8H_2O$, $6H_2O$).

extended temperature range, before transforming into a phase with 8 water molecules at 95 °C.

At a temperature of 155 °C, all interlayer water is lost and further increase of temperature leads to loss of structurally necessary water and destruction of AFm-phases. This phase can be given by the structural formula as

$$Ca_4[Al_2(OH)_{12}]^{2+}\ [CrO_4]^{2-}$$

Containing no further interlayer water. Further increase of temperature then leads to a destruction of the layered structure and a disappearance of the 0 0 l-reflections.

But even more hydration stages of AFm-phase with chromate can be given when low temperatures occur.

Establishing high relative humidities and low temperatures additional water enters the interlayers and even higher hydration stages can be established. At 5 °C and 100% relative humidity a $d_{(00l)}$ of $c'=10.45$ Å can be measured. With increasing temperatures also a $c'=10.34$ Å can be measured. A hydration stage of 14 molecules of water at 25 °C is stable at 76% relative humidity.

The various water contents of the compound $Ca_4[Al_2(OH)_{12}]^{2+}$ $[CrO_4 \cdot nH_2O]^{2-}$ and their stability areas and conditions are summarized in Table 3. Assumptions of the water contents 16 and 18 can be made by extrapolation of the increase of layer distance with temperature, because there is some overlapping in the determination of interlayer and surface water.

Some of these hydrates could not be obtained in pure state, but were always accompanied by the next hydrations stages, due to very narrow temperature stability regions (11, 10 interlayer water molecules).

In summary, depending from relative humidities and temperatures, monochromate shows 9 different hydration stages before structural necessary water originated from the OH-groups in the main layer is lost.

The results of the IR-spectroscopical investigation of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ are given in Appendix A2 and B1. The broad absorption bands of water, OH and chromate dominate the IR-diagram.

3.2. *Investigations in the system $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$–$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot nH_2O$*

The investigations in the system were performed using starting compositions of $(3-x)CaO+CA+(x)CaCrO_4+nH_2O$ with ratios of $0<x<1$ with intervals of 0.1.

Table 3
Water contents, preparation conditions and spacing of $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$.

Drying conditions	Relative humidity (%)	T (°C)	c' (Å)	Total Water content of compound $n=$
–	100	≤ 5	10.45	18?
–	100	$5<T<25$	10.34	16?
–	100	25	10.24	14
Satur. KCl-solution	86	25	10.24	14
Satur. NaCl-solution	76	25	10.24	14
Satured $CaCl_2$-solution	35	25	9.74	12
60%-sulphuric acid	17	25	9.15	11?
60%-sulphuric acid	17	25	8.79	10?
60%-sulphuric acid	17	25	8.40	9

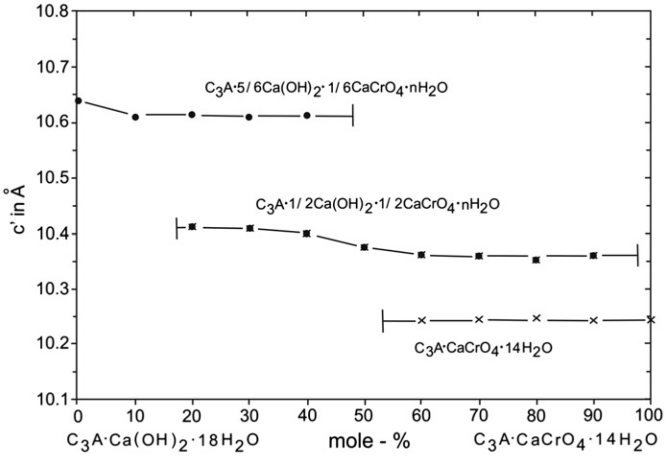


Fig. 3. Course of spacing c' of phases in the system $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 14H_2O$–$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 18H_2O$ at 100% relative humidity at 23 °C.

The mixtures were shaken continuously for 1 month at 25 °C. The phase relations are described at 100% relative humidity and 35% relative humidity in Figs. 3 and 4, showing different hydrates depending on rel. humidity. On drying, from 100% rel. humidity to 35% rel. humidity all phases and solid solutions in the system, loose some structurally not necessary water from the interlayers. Due to the loss of some interlayer water the spacings c' of occurring phases and solid solutions in the system are reduced on drying from 100% to 35% relative humidity (Figs. 3 and 4).

In the system $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O-3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$ there is some restricted solid solution as with increasing chromate presence, $CrO_4{}^{2-}$ is incorporated in TCAH up to 17 mol% by exchange of 2 OH against $CrO_4{}^{2-}$. This phenomena can be followed by a slight decrease of the relevant lattice parameter c_o and therefore only one phase is present in the system showing some solid solution to the boundary composition of $3CaO \cdot Al_2O_3 \cdot 1/6CaCrO_4\ 5/6Ca(OH)_2 \cdot 12H_2O$. The relevant compositions therefore can seen directly in Figs. 3 and 4. At chromate concentrations exceeding 17 mol%, two phases coexist in the system: $3CaO \cdot Al_2O_3 \cdot 1/6CaCrO_4 \cdot 5/6Ca(OH)_2 \cdot 12H_2O$ (17 mole% chromate) and a compound with a composition of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$, which is called hemichromate.

At chromate contents of $2OH/CrO_4=1$ an intermediate compound, hemichromate, with a composition of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ crystallizes as a single phase in

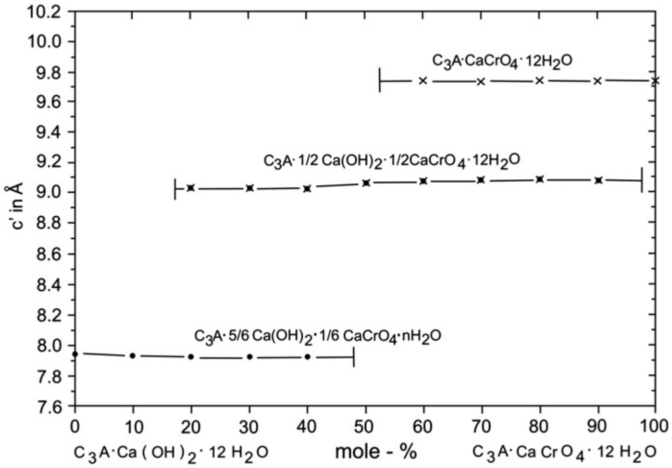


Fig. 4. Course of spacing c' of phases in the system $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$–$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$ at 35% relative humidity at 23 °C temperature increase: 10 °C/min, atmosphere: air.

the system $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O - 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$. This compound has the structural formula

$$Ca_4[Al_2(OH)_{12}]^{2+} \cdot [1/2CrO_4OH] \cdot nH_2O^{2-}$$

The course of lattice parameter c' implies some phase broadness of this compound. In the chromate-rich part of the system, exceeding 50 mol% chromate a miscibility gap between hemichromate and monochromate exists, because of the coexisting phases $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ (monochromate) and $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ (hemichromate). The new intermediate phase $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ (hemichromate) in the system $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$–$3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot nH_2O$ and its properties are described in detail in Section 3. Relevant variable water contents of these phases depend on composition, temperature and relative humidity. The variation of water contents in the solid solution series is given for 100% rel. humidity and 35% relative humidity. The different lower hydration stages of AFm-phases can be rehydrated to their higher hydrated phases completely, because the water in the interlayers is structurally not necessary.

In Figs. 3 and 4 the phase relations are shown giving similar AFm-phases, but different water contents of the interlayers. Some dehydration of the interlayers of AFm-phases occur when dried from 100% rel. humidity to 35% rel. humidity due to loss of interlayer water.

The systems clearly shows an intermediate compound with the composition $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ with a decreasing lattice spacing on drying. This phase was purely synthesized, its properties determined and the water contents, depending on relative humidity, described.

The phase relations in the system $CaO - Al_2O_3 - CrO_4{}^{2-} - H_2O$ show 2 main phases and a solid solution (no hydration stages included) which are summarized in Table 4.

Obviously also the intermediate compound $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ shows some chemical broadness due to some variation in lattice parameter c_o in the OH-rich part of the system due to some variations in the molar ratios of OH and chromate in the interlayer.

Table 4
Main chromate containing AFm-phases (monochromate, hemichromate) and solid solution of AFm by incorporation of chromate in TCAH at 35% relative humidity.

(1) $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot 12H_2O$
(2) $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$
(3) $3CaO \cdot Al_2O_3(0–0.17) \cdot CaCrO_4(1–0.83) \cdot Ca(OH)_2 \cdot 12H_2O$ $(0 \leq x \leq 0.17)$

Table 5
Chemical analysis of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ at 25 °C and 35% r.h.

Oxide	Weight % (theor.)	Weight % (measured)
CaO	36.8	37.0
Al_2O_3	16.7	16.5
CrO_3[a]	8.3	8.4
H_2O	38.2	38.0
$\sum$	100	99.9

[a] CrO_3 recalculated from chromate determination.

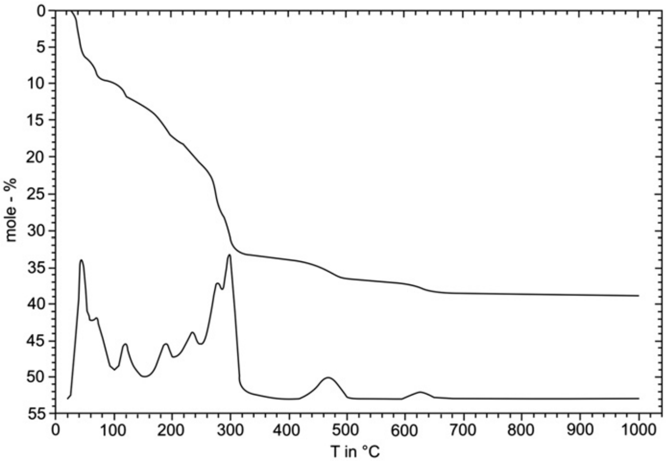


Fig. 5. TG-curve of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$, temperature increase: 2°/min (TG), 5 °C (DTG); gas: N_2 of 35% r.h.

3.3. *Description of intermediate phases $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$*

At 25 °C and 100% rel. humidity a hydrate with ~14 molecules of water is stable, showing a spacing of $c' = 10.276$ Å. This compound dehydrates at 35% r.h. to a phase with a composition of 12 H_2O-molecules and a lattice spacing of 9.062 Å. The chemical composition was determined from a compound dried at 35% rel. humidity and precisely a molar ratio of 0.5 $(OH)_2/CrO_4$ was obtained, as shown in Table 5.

The thermoanalytical investigations of this compound show clearly that also different water stages of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ (hemichromate) exist. In Appendix A3 the DSC and in Figs. 5 and 6 the TG and the corresponding course of high temperature X-ray d_{001} changes are shown. The corresponding interpretation of the various hydrates is given in Table 6.

Water contents and interpretation of thermoanalysis of the compound $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ are given in Table 6.

No X-ray patterns with distinct and definite peaks could be obtained of the lower hydrates having 8 and 6 molecules of water—they could only be determined clearly by thermogravimetric analysis.

A higher hydration stage of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ present at 100% rel. humidity with a d_{001} of 10.37 Å also was identified. The water content is about 14 water molecules.

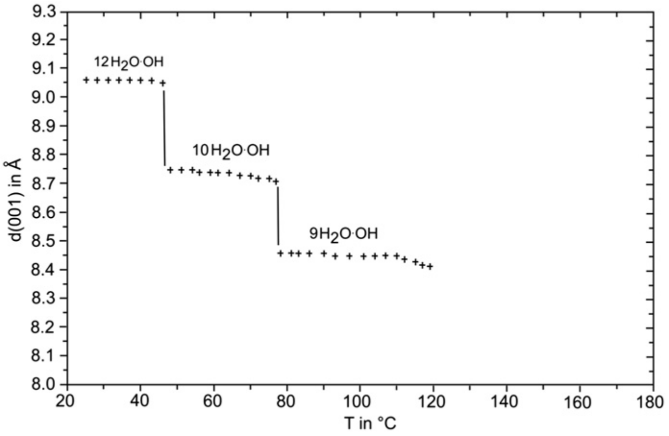


Fig. 6. Course of $d_{(001)}$-values of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ with increasing temperature using high temperature X-ray equipment. ($n = 12H_2O$, $10H_2O$, $9H_2O$).

Table 6
Water stages of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ and temperature stability regions.

T (°C)	Weight-loss (%)	d_{001} (Å)	Total water content of compound $n=$
25	–	9.06	$12H_2O \cdot OH$
50	6.1	8.75	$10H_2O \cdot OH$
75	9.1	8.46	$9H_2O \cdot OH$
125	11.9		$8H_2O \cdot OH$
300	17.7		$6H_2O \cdot OH$
310	32.5	Loss of OH from interlayer	
500	36.4	Destruction of main layer	
650	38.4	Reduction of Cr^{6+} combined with production of O_2	
1000	38.9		

The infrared spectra of $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot 12H_2O$ is given in Appendix A4 and measured frequencies and their interpretation summarized in Table B2.

4. Sorption experiments

Chromate can be easily bound into AFm-phases, therefore some interlayer exchange experiments were included in this study. A replacement of $2OH^-$ in the solid phase by $CrO_4{}^{2-}$ from solution can take place.

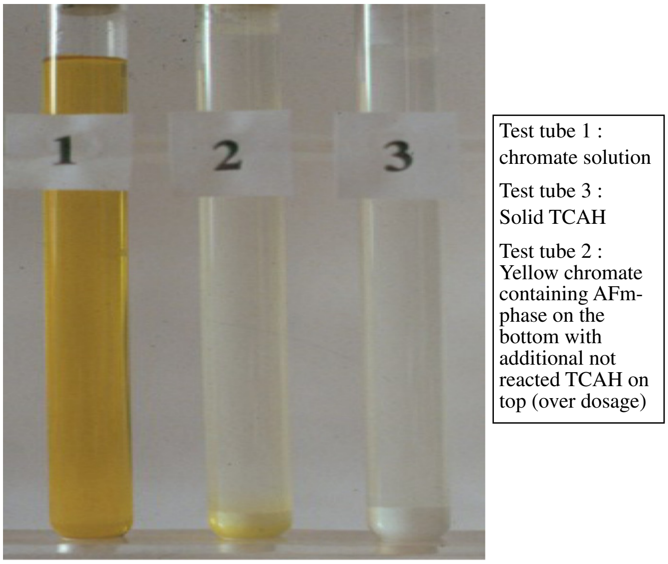
Chromate is incorporated easily in TCAH as it is shown in Fig. 7. In case of mixing 20 ml of a chromate solution (3000 g/l) with some solid, freshly prepared TCAH (4 g dried at 23 °C) shaken continuously for 2–10 min, an incorporation of chromate from solution in the interlayer of the lamellar phases takes place. After clarifying and settling of the solid, the initial yellow solution, containing chromate, has changed to clear and transparent. The residual concentration of the solution has now dropped to < 0.2 g/l chromate. The solid precipitate now contains all the chromate forming different AFm-solid solutions with yellowish colours. An interlayer exchange of the AFm-phases has taken place:

$$OH^- \leftarrow \rightarrow CrO_4{}^{2-}$$

The new formed solid chromate containing phases with AFm-structures are solid solutions with compositions as

$$CaO \cdot Al_2O_3(1-x)CaCrO_4(x) \cdot Ca(OH)_2 \cdot nH_2O$$

with $0 \leq x \leq 1$



Test tube 1 :
chromate solution

Test tube 3 :
Solid TCAH

Test tube 2 :
Yellow chromate containing AFm-phase on the bottom with additional not reacted TCAH on top (over dosage)

Fig. 7. Sorption of chromate in TCAH forming TCAH- AFm-chromate solid solutions (test tube 2 showing yellow chromate incorporated in TCAH and unreacted white TCAH on top)-solution completely clear (chromate < 0.2 mg/l)).

Table 7
Removal of chromate due to fixation in TCAH (mg/l in solution).

Time for sorption experiment in hours	Addition of 0.1 molar Na_2CrO_4-solution	Addition of 0.05 molar Na_2CrO_4-solution	Addition of 0.1 molar Na_2CrO_4-solution
0	1560	780	156
1	2.2	1.4	0.18
5	2.0	1.2	0.16
10	1.7	1.1	0.15
24	1.6	0.9	0.14
72	1.3	0.75	0.12

Due to the non-equilibrium conditions of the rapid exchange different chromate containing phases can occur, as there are monochromate, hemichromate and low chromate-containing solid solutions with TCAH (tetra calcium aluminate hydrate).

The overdosage of TCAH over the necessary uptake of chromate, test tube 2 still contains some original TCAH (white colour), which does not uptake any chromate from the solution (horizontal bar showing the borderline between chromate containing AFm (yellow) and TCAH. Many different chromate exchange reactions using mixtures of AFm-phases and other sorption materials were described in detail in [44–47].

Some details of the uptake of chromate in TCAH from a Na_2CrO_4-solution with water/solid ratio$=15$ is described in Table 7.

It is clearly demonstrated that TCAH can be used at lower chromate concentrations to get a chromate reduction in solution below 0.2 mg/l after sorption times of less than 1 h.

5. Summary and discussion

Chromate can be incorporated in TCAH phases. The newly synthesized AFm-phases are

1. $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$
2. $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$
3. $3CaO \cdot Al_2O_3 \cdot 1/6CaCrO_4 \cdot 5/6Ca(OH)_2 \cdot nH_2O$

These lamellar phases do have various discrete water contents depending on tha type of anion, composition, temperature and relative humidity.

Also some partial solid solution series exist in the region of the system
$3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O - 3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot nH_2O$.

The composition range can be given by

$$CaO \cdot Al_2O_3(0-x)CaCrO_4(1-x) \cdot Ca(OH)_2 \cdot 12H_2O$$

$$(0 < x < 0.17)$$

The intermediate phase $3CaO \cdot Al_2O_3 \cdot 1/2CaCrO_4 \cdot 1/2Ca(OH)_2 \cdot nH_2O$ also shows some compositional broadness in the OH-rich part of the system. These chromate-containing AFm-phases can be formed during a technical sorption experiment for chromate immobilization.

Depending on the kinetics of incorporation, chromate also can be incorporated in ettringite-like phases, which were not investigated in this study [30,31,40]. Investigations in carbonate containing AFm-systems prove, that monocarbonate and monochromate are completely immiscible and do coexist in the relevant systems [40]. Chromate containing AFm-phases show many different hydration stages which mainly can be identified by their 0 0 l-reflections, due to preferential orientation of plately phases. X-ray investigations therefore are to be performed by definite control of relative humidity and temperature, otherwise misinterpretation of phases is highly possible.

Figs. 8 and 9 show hexagonal shaped AFm-phases with chromate incorporation.

Increasing temperatures may also lead to some transformation reactions of tetracalcium aluminate hydrate into portlandite and hydrogarnet.

Macroscopically, chromate containing AFm-phases are bright yellow in colour, with an indication of deeper yellow with increasing chromate contents.

These phases therefore can be used as a potential sink for chromate from solutions. Some extensive work showing the removal of chromate from solution by AFm-phases was performed in [25–27]. The phases precipitating in these systems now can be identified, because the characterization and the properties were determined. In cementitious systems, the chromate can be incorporated basically in ettringite, which can be transformed to AFm-phases during carbonation reactions. Chromate therefore can be bound in a cementitious systems in AFt and AFm-phases. The prove of incorporation of Cr^{6+} in definite cement phases, including all different hydration stages, can now be performed by X-ray analysis. The incorporation of Cr^{3+} in similar layered structures was also described in [43].

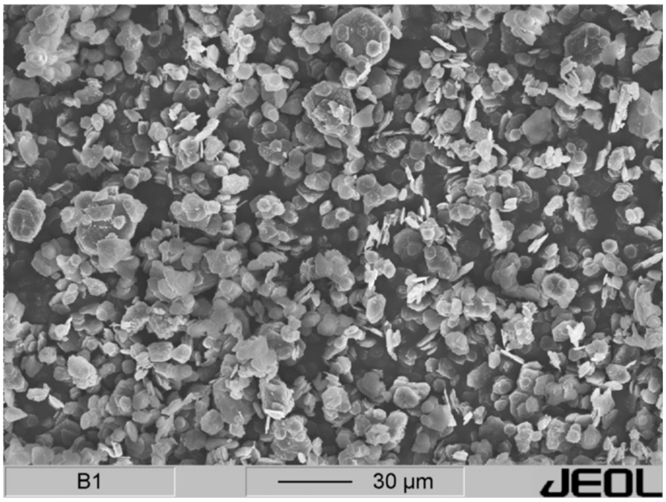


Fig. 8. $3CaO \cdot Al_2O_3 \cdot CaCrO_4 \cdot nH_2O$ (monochromate) at 25 °C.

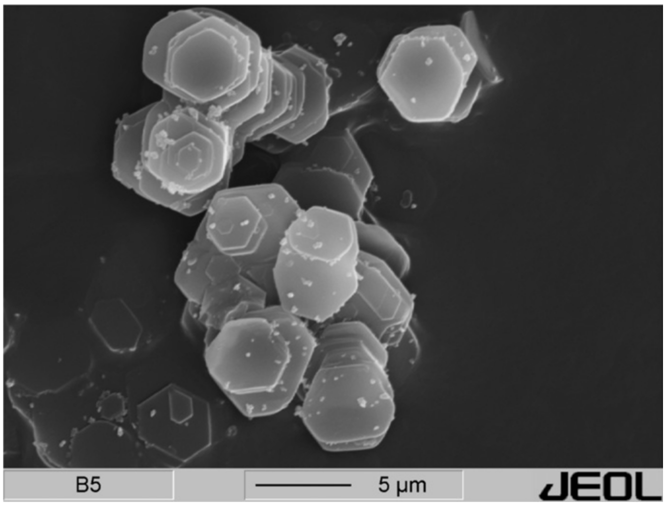


Fig. 9. Solid solution of $3CaO.Al_2O_3.CaCrO_4.nH_2O$ (monochromate) with TCAH (tetra calcium aluminium hydrate) (small hydrogarnets on top of the lamellar phases due to conversion of TCAH into $CH+C_3AH_6$).

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.10.022.

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