THE IMPACT OF Li_2CO_3 AND SOME OTHER ACCELERATORS ON THE CAC HYDRATION

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Abstract

The setting of cement pastes containing calcium aluminate cements (CACs) can be accelerated by additions of selected alkali metal or alkaline earth metal compounds. In this work, the accelerating effects of Li_2CO_3, $MgCO_3$ and a sodium alginate are studied on basis of quantity-dependent changes in the phase assemblage of hydrated CAC samples (water cement ratio w/c = 1). The samples were hydrated for 24 hours and then used to measure X-ray diffraction data. In quantitative phase analyses, employing the measured data, the sample compositions were determined.

Generally, the first hydrate phases which crystallize during the CAC hydration at room-temperature are C_2AH_8 ($2CaO·Al_2O_3·8H_2O$), CAH_{10} ($CaO·Al_2O_3·10H_2O$) and AH_3 ($Al(OH)_3$). In samples whose dry mixtures possess a Li_2CO_3 content of 0.0 to 0.03 wt%, all three hydrate phases crystalize during the initial hydration. The CAH_{10} content in these samples, however, decreases drastically with increasing Li_2CO_3 addition. In samples with a Li_2CO_3 content of 0.04 wt% or higher, the CAH_{10} phase is absent. The phase amounts of C_2AH_8, AH_3, C_3AH_6 and a Li_2CO_3-containing layered double hydroxide (LDH) also depend on the added amount of Li_2CO_3. While CAC samples containing ~0.1 wt% Li_2CO_3 develop particularly high amounts of C_2AH_8 during hydration, a further increase of the Li_2CO_3 amount is associated with a decrease in the C_2AH_8 amount and an increase in the C_3AH_6 amount. The inversely correlated formation of C_2AH_8 and C_3AH_6 seems to result from a transition of C_2AH_8 into C_3AH_6.

Compared to additions of Li_2CO_3, additions of $MgCO_3$ or sodium alginate induce much smaller changes in the phase composition of the hydrating CAC and are not associated with a suppression of the CAH_{10} formation.

Introduction

Although Li_2CO_3 and other lithium-containing salts are widely used to shorten the hardening time of cement pastes, the origin of the accelerating effect caused by these compounds is still unclear. Possibly, the accelerating effect is partly driven by an initial formation of a layered double hydroxide (LDH) [1, 2]. However, evidence for the influence of the LDH phase on the formation of typical hydrate phases, like AH_3, C_2AH_8, CAH_{10} and C_3AH_6, is still lacking.

Apart from lithium-containing salts, also other metal salts can react with aluminum hydroxide to form LDH compounds [3-6]. However, none of these compounds are known to possess a similar strong influence on the hydration process of CACs as the Li-containing compounds. The involvement of the LDH phase in the CAC hydration still needs closer examination to understand the function of the LDH phase in the hydration process. Interestingly, C_2AH_8 itself represents a LDH phase [7]. In hydrated samples of Li_2CO_3-containing CACs, the C_2AH_8 formation is often favored over the formation of the CAH_{10} phase, leading frequently even to a complete absence of the CAH_{10} phase in the hydrated CAC [1, 2]. As the crystal structure of C_2AH_8 can be formally derived from the Li–Al–CO_3 LDH phase by ion exchange reactions, the rather sluggish reconstructive formation of CAH_{10} is possibly kinetically outperformed by a faster formation of C_2AH_8.

Although the C_2AH_8 formation might be activated by the LDH phase, several other factors, especially the pH value and the concentrations of $Al(OH)_4^-$ and Ca^{2+} ions, influence the CAC hydration as well [1]. Recently, it was revealed that the setting process of CACs can also be accelerated by additions of sodium alginate [8], a product derived from natural algae. In the dissolved alginate, long molecular chains of polysaccharides can bind Ca^{2+} ions in chelate complexes. This entrapment seems to be the key feature by which the alginate influences the CAC hydration [8].

Experimental

Materials

For the hydration experiments a commercially available cement was used containing the cementitious phases CA (~ 94.5 wt%), CA_2 (~ 3.5 wt%) and $C_{12}A_7$ (~ 2 wt%). Lithium carbonate (Li_2CO_3, 99 wt%, Merck), magnesium hydroxycarbonate ($MgCO_3·xH_2O$, 99 wt%, Merck), in this work abbreviated by $MgCO_3$, as well as sodium alginate (Vivapur, J. Rettenmaier und Söhne) were added in the CAC in amounts up to 1.0 wt% to investigate the influence of these additions on the CAC hydration.

Ultrasonic measurements

The setting of hydrated CAC samples was probed by measuring the time needed by ultrasonic signals to travel through the sample using an ultrasonic device of UltraTest (Ultrasonic – Tester BP7). Transmitter and receiver sensors were placed in each measurement 30 mm apart from each other to allow for a better comparability of the measurements. The samples were prepared by mixing 50 g of each dry mixture (containing the CAC and the accelerator) or the pure CAC with 50 g demineralized water in a closed vessel.

Hydration experiments, samples for XRD measurements

Samples were prepared by mixing 10 g of the pure CAC or 10 g of a dry mixture with the same amount of demineralized water in sealable, air-tight plastic bags. The dry mixtures were prepared beforehand by mixing the CAC with small amounts of the accelerators (0.0 – 1.0 wt%). After storing for 24 hours at room-temperature in an air-conditioned room, the hydrated samples were ground in a mortar and used to measure XRD patterns.

XRD measurements, phase analysis

Powder diffraction patterns of the hydrated CACs were measured in a 2θ range from 4 to 70 deg. using an X'Pert^3 diffractometer (PANalytical) equipped with a $CuK\alpha_1$ tube. Measurements were carried out in reflection mode (Bragg-Brentano geometry) with a measuring time of 17 minutes for each pattern. Peaks in the diffraction patterns were identified as reflections of the cementitious phases CA and CA_2 and of hydrate phases formed by the reaction of the CAC with water. Quantitative phase analyses were conducted by employing the computer program Jana2006 [9] using crystal structure data found in the data base COD (Crystallographic Open Database) [10] and in the literature [11, 12] (Tab. 1).

Tab. 1: Phases considered in the phase analysis. ID numbers refer to data base entries in the COD [10].

Phase		**ID number**
CA		4308075
CA_2		9014425
CAH_{10}		2103045
C_3AH_6		9001085
AH_3		9008237
C_2AH_8		3500118
Li–Al–CO_3 LDH	reference [11]	-
Mg–Al–CO_3 LDH	reference [12]	-

Influence of Li_2CO_3 additions on the properties of a CAC-containing mass and of sample bars produced from the mass

The effect of small additions of Li_2CO_3 on the flowability of a CAC-containing castable was investigated in flow tests conducted with a tabular alumina-based mass. The dry mixture of the mass was composed of 90 wt% tabular alumina, comprising different grain size ranges (Tab. 2), 10 wt% CAC and small additions of Li_2CO_3 (0-0.04 wt% with respect to the amount of the CAC in the dry mixture; 0-0.004 wt% with respect to the total weight of the dry mixture, Tab. 2). For the preparation of the mass, 2 kg dry mixture was mixed with 200 g water and stirred for 2 minutes at 140 rpm in a mortar mixer. The mass was used to determine the flowability in a flow test and to produce sample bars, whose material strengths were probed after a curing time of 24 hours.

Tab. 2: Composition of dry mixtures used to prepare tabular alumina masses containing small amounts of Li_2CO_3.

raw materials	**wt%**
Al-Tab, 1-3 mm	30
Al-Tab, 0.5-1 mm	20
Al-Tab, 0.2-0.6 mm	20
Al-Tab, 0-0.2 mm	20
CAC	10
Li_2CO_3	<0.004

Results and Discussion

Small additions of Li_2CO_3, $MgCO_3$ or sodium alginate in a CAC cause the setting of the cement paste to occur remarkably earlier than the setting of the hydrated sample prepared from the pure CAC (Fig. 1). While the addition of $MgCO_3$ or alginate results in a shortening of the induction period by about 4-7 hours, the addition of Li_2CO_3 shortens the induction period by ~12 hours.

Additions of Li_2CO_3 strongly influence the phase formation in a CAC during a hydration of 24 hours (Fig. 2, Tab. 3). For an addition of Li_2CO_3 in amounts up to 0.03 wt%, the CAH_{10} content in the hydrated CAC declines drastically. An addition of 0.04 wt% Li_2CO_3 or more precludes the CAH_{10} formation by favoring the crystallization of the hydrate phases C_2AH_8 and AH_3. The hydration of samples possessing a Li_2CO_3 content of 0.1 wt% or higher results in the formation of the C_3AH_6 phase, whose phase amounts increase with the amount of added Li_2CO_3 (Fig.2 und Tab. 3). In parallel, the increase of the C_3AH_6 amount is associated with a decrease of the phase amount of C_2AH_8. This inverse correlation of the two phase amounts might be interpreted by a development of the C_3AH_6 phase from the C_2AH_8 phase as it is described in reference [13] for CAC samples hydrated at 60°C. Another inverse correlation, comparatively less pronounced, pertains the formation of the phases AH_3 and LDH. Here, increasing Li_2CO_3 additions lead presumably to increasing amounts of LDH, decreasing concomitantly the remaining amount of AH_3.

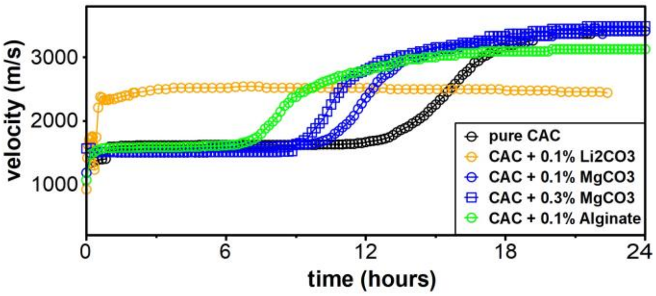

Fig. 1: Velocity of ultrasonic signals measured during hydration of different CAC samples. Colors refer to accelerators mixed in the samples.

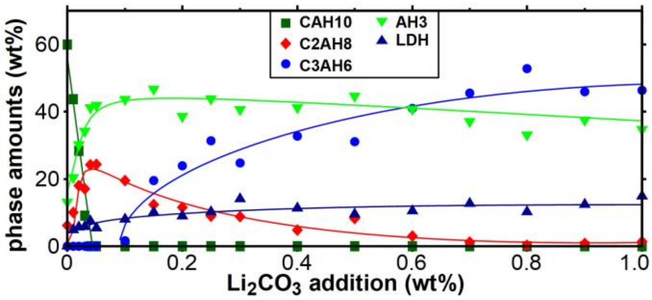

Fig. 2: Amounts of hydrate phases formed by hydration of mixtures of a CAC with different amounts of Li_2CO_3. Phase amounts refer to the phase composition determined after a sample hydration for 24 h (Tab. 3). Coloured lines are guides to the eye.

Tab. 3: Phase compositions of hydrated CAC samples given for different amounts of Li_2CO_3 mixed into the samples before hydration. The compositions were determined after a sample hydration of 24 h. Values in wt%.

added Li_2CO_3	**Phase composition**						
(wt%)	**CA**	**CA_2**	**CAH_{10}**	**C_2AH_8**	**C_3AH_6**	**AH_3**	**LDH**
0.00	17.9	2.1	60.0	6.2	0.0	13.2	0.0
0.01	17.4	3.5	43.7	10.0	0.0	20.5	4.8
0.02	17.4	5.3	28.3	18.0	0.0	30.3	5.7
0.03	30.6	3.6	9.1	17.1	0.0	34.2	5.3
0.04	23.5	3.8	0.0	24.2	0.0	41.2	7.4
0.05	20.5	7.2	0.0	24.4	0.0	41.9	5.4
0.10	23.7	3.3	0.0	19.6	1.7	43.7	8.0
0.15	9.4	1.9	0.0	12.4	19.6	46.7	10.0
0.20	14.1	2.7	0.0	11.6	23.9	38.7	8.9
0.25	3.9	1.6	0.0	9.0	31.4	43.9	10.2
0.30	10.3	1.6	0.0	8.8	24.8	40.7	14.0
0.40	8.0	1.8	0.0	4.8	32.8	41.2	11.3
0.50	6.6	1.4	0.0	8.2	31.1	44.7	9.5
0.60	3.5	1.2	0.0	3.1	41.0	40.8	10.5
0.70	2.5	1.2	0.0	1.2	45.5	37.1	12.6
0.80	2.9	0.7	0.0	0.3	52.8	33.1	10.2
0.90	2.4	0.7	0.0	0.9	45.9	37.6	12.4
1.00	2.1	0.6	0.0	1.4	46.4	34.8	14.8

The amount of unreacted CA phase increases for the addition of small amounts of Li_2CO_3 (< 0.1 wt%) and decreases for additions of Li_2CO_3 larger 0.1 wt%, following a similar trend as the C_2AH_8 formation (Tab. 3). Possibly, the presence of the C_2AH_8 phase might influence the amount of CA phase remaining in the hydrated sample, e.g. by an encapsulation of CAC grains.

As C_2AH_8 is one of the first phases crystallizing, it should also influence the initial strength formation in the sample. However, CAC samples containing 0.1 wt% Li_2CO_3 set already ~1 hour after mixing with water (Fig. 1). At that time, only small amounts of the crystalline hydrate phases C_2AH_8 and AH_3 reside relatively large amounts of the CA phase, indicating the initial hardening of the sample to be more influenced by a binding of the CA grains through an amorphous phase.

Compared to Li_2CO_3 additions, $MgCO_3$ or alginate show lower effects on the formation of the hydrate phases in hydrating CAC. Although increases in $MgCO_3$ additions result in small decreases of the CAH_{10} content of the CAC after a hydration of 24 hours, the CAH_{10} phase is with a phase amount of ~60 wt% the dominating hydrate phase in the sample. An increase of the added amount of $MgCO_3$ leads to small increases in the phase amounts of the LDH phase, but a less clear trend for the changes in the phase content of C_2AH_8 and AH_3 (Fig. 3, Tab. 4). As the amounts of C_3AH_6 are quite low in the hydrated samples with high CAH_{10} contents, it seems that C_3AH_6 just develops from the C_2AH_8 phase and not from CAH_{10}, corroborating the results of Hueller et al. [13].

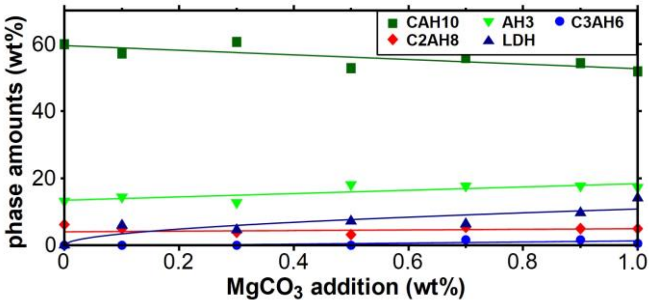

Fig. 3: Amounts of hydrate phases formed by hydration of mixtures of a CAC with different amounts of $MgCO_3$. Phase amounts refer to the phase composition determined after a sample hydration of 24 h (Tab. 4). Coloured lines are guides to the eye.

Tab. 4: Phase compositions of CAC samples given for different amounts of $MgCO_3$ added to the samples before hydration. The compositions were determined for a sample hydration over 24 h. Values in wt%.

added $MgCO_3$	**phase composition**						
(wt%)	**CA**	**CA_2**	**CAH_{10}**	**C_2AH_8**	**C_3AH_6**	**AH_3**	**LDH**
0.00	17.9	2.1	60.0	6.2	0.0	13.2	0.0
0.10	14.8	2.9	57.3	4.9	0.0	14.4	5.9
0.30	16.3	1.6	60.6	3.9	0.1	12.8	4.5
0.50	17.1	1.7	52.8	3.2	0.0	18.1	7.2
0.70	10.2	3.1	55.8	5.4	1.6	17.7	6.8
0.90	10.5	1.8	54.3	5.0	1.7	17.8	9.6
1.00	11.0	0.1	51.9	5.0	0.6	17.4	14.1

Tab. 5: Phase compositions of CAC samples given for different amounts of alginate added in the samples before hydration. The compositions were determined after a sample hydration of 24 h. Values in wt%.

added alginate	**phase composition**					
(wt%)	**CA**	**CA_2**	**CAH_{10}**	**C_2AH_8**	**C_3AH_6**	**AH_3**
0.00	17.9	2.1	60.0	6.2	0.0	13.2
0.10	14.8	4.8	61.5	4.7	1.5	12.6
0.50	11.8	3.7	51.1	10.8	2.5	20.0
1.00	15.8	2.4	52.0	12.4	2.6	14.8

Effect of Li_2CO_3 additions on the flowability of a CAC-containing mass and the influence on the green strengths

By increasing the Li_2CO_3 content in a CAC-containing tabular alumina-based mass, the flowability strongly decreases (Tab. 6). The amount of added Li_2CO_3 also influences the materials strengths of sample bars produced from the mass. In accordance with findings of Matusinović et al. [2], higher Li_2CO_3 contents in CAC samples affect lower material strengths (Tab. 6).

As Li_2CO_3 additions induce large changes in the phase composition of hydrating CAC samples (Tab. 3, Fig 2), they can affect crucial changes in the microstructure and influence the green strength of the samples. The comparatively high green strength of samples containing large amounts of the CAH_{10} phase can be attributed to a crystallization of the phase in a bulky mass. Crystals of C_2AH_8, in contrast, grow to rather thin platelets accounting for a higher brittleness of the hydrated CAC.

Tab. 6: Influence of the Li_2CO_3 content on the flow of a tabular alumina mass (Tab. 2) and the cold modulus of rupture (CMOR) as well as cold crushing strength (CCS) of sample bars produced from the mass.

Li_2CO_3 addition (wt%)	**flow**	**CMOR (MPa)**	**CCS (MPa)**
0.00	142%	5.25	35.6
0.01	133%	4.84	29.3
0.02	127%	5.24	25.1
0.03	78%	5.17	21.5
0.04	55%	3.85	13.0

Conclusions

Small additions of Li_2CO_3 strongly influence the phase formation during the CAC hydration. By the addition of $MgCO_3$ or sodium alginate, which can also accelerate the setting of CACs, comparatively smaller changes in the phase assemblage is provoked.

Samples mixed with different amounts of Li_2CO_3 and hydrated according to a water to cement ratio w/c = 1 formed CAH_{10} only when Li_2CO_3 was added in amounts below 0.04 wt%. In these samples, the CAH_{10} amount was found to decrease drastically with increasing amount of added Li_2CO_3. By hydration of CAC samples containing Li_2CO_3 in an amount of 0.04 wt% or higher, the phases C_2AH_8, AH_3, C_3AH_6 as well as a LDH phase formed, however, no CAH_{10}.

While CAC samples mixed with ~0.1 wt% Li_2CO_3 develop particularly high amounts of C_2AH_8 during the hydration, higher Li_2CO_3 additions result in a decrease of the C_2AH_8 amount and an increase of the C_3AH_6 amount. The inverse correlation of these phase amounts can be interpreted by a transition of C_2AH_8 into C_3AH_6, which seems to depend on the amount of added Li_2CO_3.

In some further tests, the influence of Li_2CO_3 on the flowability of a CAC-containing tabular alumina mass was probed. It was found that the flowability decreases significantly if small amounts of Li_2CO_3 were added in the dry mixture of the mass. The green strength of sample bars produced from the mass also decreases through an increase of the Li_2CO_3 amount.

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