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Influence of citric acid on the hydration of Portland cement

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ABSTRACT

Citric acid can be used to retard the hydration of cement. Experiments were carried out to investigate the influence of citric acid on the composition of solid and liquid phases during cement hydration. Analyses of the solid phases showed that dissolution of alite and aluminate slowed down while analyses of the pore solution showed that citric acid was removed almost completely from the pore solution within the first hours of hydration. The complexation of the ions by citrate was weak, which could also be confirmed by thermodynamic calculations. Only 2% of the dissolved Ca and 0.001% of the dissolved K formed complexes with citrate during the first hours. Thus, citric acid retards cement hydration not by complex formation, but by slowing down the dissolution of the clinker grains. Thermodynamic calculations did not indicate precipitation of a crystalline citrate species. Thus, it is suggested that citrate sorbed onto the clinker surface and formed a protective layer around the clinker grains retarding their dissolution.

1. Introduction

Citric acid retards the hydration of Portland cements or its constituents. Tinnea and Young [1] and Singh et al. [2] showed that citric acid has a retarding effect on the hydration in the system C_3A–gypsum–portlandite–water, while Stadelmann [3] showed that citric acid has the same effect on the hydration of C_3S. Wilding et al. [4] and Ramachandran and Lowery [5] investigated the effect of citric acid, and citrate respectively, on Portland cement and showed by heat evolution rates that the hydration of Portland cement is retarded. Other investigations aimed to understand the mechanisms of the retardation. Pore solutions (collected after different times of hydration) have been analyzed for ion concentrations and organic carbon. The zeta potential as well as the composition of the hydrated solid phases have been studied [6–8]. Singh et al. [6] found that the zeta potential of cement decreases with increasing amounts of citric acid added, which was explained by the adsorption of citrate ions onto the positively charged surfaces of the Portland cement grains. Schwarz [7] concluded that citrate increases the dissolution rate of the ferrite phase. Smillie and Glasser [8] found that citric acid (15.6 mmol/l) is removed almost quantitatively from the cement pore water within the first hour of cement hydration. Schwarz et al. [9] postulated that citrate forms stable complexes with polyvalent metal cations, which were claimed to affect both, the solution and the (ferro-)aluminate-surface chemistry.

Thermodynamic modeling has been used to calculate the composition of pore solution and solid phases after different hydration times, which gives an insight into the chemical processes during cement hydration [10]. Lothenbach et al. [11] have also studied the influence of temperature on the hydration products of cement by thermodynamic modeling and have shown that thermodynamic modeling can be a powerful tool to predict the phase assemblage during cement hydration.

In the title study the influence of citric acid on the hydration of Portland cement was studied. The changes in the composition of the liquid and solid phase as a function of time and amount of citric acid added were investigated. Thermodynamic modeling was used to calculate the extent of complex formation of the dissolved ions and the results were compared with the experimentally determined concentrations.

2. Materials and methods

2.1. Experiments

All experiments were carried out using an ordinary Portland cement (OPC), CEM I 42.5 N, at 20 °C. The composition of the unhydrated cement and the calculated amount of the clinker phases are shown in Table 1. The chemical composition of the unhydrated cement was determined by X-ray fluorescence (XRF).

Cement pastes were prepared with a w/c of 0.4 by adding 1 kg cement to 400 g distilled water. To study the retardation of citric acid ($C_6H_8O_7$) on the hydration, three different concentration of citric acid were added to the mixing water, equivalent to 0.1, 0.4 and 0.5 wt.% of cement resulting in concentrations of citric acid of 13, 52 and 65 mmol/l. The solutions were mixed for 3 min with the cement according to EN 196-1. The pastes were stored in 0.5 l PE bottles (0.1 l for fresh cement

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Table 1
Composition of the OPC used (CEM I 42.5 N)[a].

Chemical analysis		Normative phase composition[b]	
	g/100 g		g/100 g
SiO_2	19.6	Alite	50.0
Al_2O_3	4.60	Belite	18.5
Fe_2O_3	2.90	Aluminate	7.3
CaO	62.4	Ferrite	8.8
MgO	1.60	CaO	0.46
SrO	0.06	$CaCO_3$	4.8
K_2O	0.97	$CaSO_4$[c]	4.3
Na_2O	0.12	K_2SO_4[e]	1.4
CaO (free)	0.46	Na_2SO_4[e]	0.08
CO_2	2.11	SrO	0.06
SO_3	3.25	K_2O[d]	0.24
Readily soluble alkalis[e]		Na_2O[d]	0.09
K_2O	0.30	MgO[d]	1.6
Na_2O	0.012	SO_3[d]	0.05

Blaine surface area: 316 m^2/kg. Ignition loss: 2.7 g/100 g.

[a] The OPC used contained 0.2% $FeSO_4 \cdot 7H_2O$ as chromate reducing agent.

[b] Calculated from the chemical analysis.

[c] Present as anhydrite (1.8 g/100 g), hemihydrate (1.3 g/100)g, and gypsum (1.6 g/100 g).

[d] Present as solid solution in the major clinker phases (distributed according to Table 1.3 in [31]).

[e] Readily soluble alkalis were calculated from the concentrations of alkalis measured in the solution after 5 min agitation at a w/c of 10.

Table 2
Thermodynamic data used to consider citrate-complexes (H_3cit = citric acid).

Species	Reaction	log K_{S0}	Reference
Aqueous			
$Hcit^{2-}$	$Hcit^{2-} \leftrightharpoons cit^{3-} + H^+$	6.36	[15]
H_2cit^{1-}	$H_2cit^- \leftrightharpoons Hcit^{2-} + H^+$	4.78	[15]
H_3cit^0	$H_3cit^0 \leftrightharpoons H_2cit^-$	3.13	[15]
Mgcit-1	$Mgcit^- \leftrightharpoons Mg^{2+} + cit^{3-}$	4.81	[15]
$MgHcit^0$	$MgHcit^0 \leftrightharpoons Mg^{2+} + Hcit^{2-}$	2.60	[15]
MgH_2cit^+	$MgH_2cit^+ \leftrightharpoons Mg^{2+} + H_2cit^-$	1.31	[15]
$Cacit^-$	$Cacit^- \leftrightharpoons Ca^{2+} + cit^{3-}$	4.80	[15]
$CaHcit^0$	$CaHcit^0 \leftrightharpoons Ca^{2+} + Hcit^{2-}$	2.92	[15]
CaH_2cit^+	$CaH_2cit^+ \leftrightharpoons Ca^{2+} + H_2cit^-$	1.53	[15]
$Kcit^{2-}$	$K^+ + cit^{3-} \leftrightharpoons Kcit^{2-}$	1.03	[32]
K_2cit^-	$2\ K^+ + cit^{3-} \leftrightharpoons K_2cit^-$	1.39	[32]
$Nacit^{2-}$	$Na^+ + cit^{3-} \leftrightharpoons Nacit^{2-}$	1.00	[32]
Na_2cit^-	$2Na^+ + cit^{3-} \leftrightharpoons Na_2cit^-$	1.81	[32]
$AlHcit^+$	$Al^{3+} + Hcit^{2-} \leftrightharpoons AlHcit^+$	4.70	[33]
$Alcit^0$	$AlHcit^+ \leftrightharpoons Alcit^0 + H^+$	−2.50	[33]
$AlcitOH^-$	$Alcit^0 \leftrightharpoons AlcitOH^- + H^+$	−3.40	[33]
$Fe(III)cit^0$	$Fe^{3+} + cit^{3-} \leftrightharpoons Fe(III)cit^0$	7.67[a]	[16]
$Fe(III)citOH^-$	$Fe^{3+} + cit^{3-} + H_2O \leftrightharpoons Fe(III)citOH^- + H^+$	5.48[a]	[16]
$Fe(III)(cit)_2^{3-}$	$Fe^{3+} + 2cit^{3-} \leftrightharpoons Fe(III)(cit)_2^{3-}$	11.64[a]	[16]
$Fe(III)(cit)_2H^{2-}$	$Fe^{3+} + 2cit^{3-} + H^+ \leftrightharpoons Fe(III)(cit)_2H^{2-}$	14.84[a]	[16]
$Fe(III)(cit)_2OH^{4-}$	$Fe^{3+} + 2cit^{3-} + H_2O \leftrightharpoons Fe(III)(cit)_2OH^{4-} + H^+$	7.51[a]	[16]
Solids			
$H_3cit(cr)$	$H_3cit(H_2O)(cr) \leftrightharpoons H_3cit^0 + H_2O$	−1.33	[15]
$Ca_3cit_2(H_2O)_4(cr)$	$Ca_3cit_2(H_2O)_4(cr) \leftrightharpoons 3Ca^{2+} + 4H_2O + 2cit^{3-}$	1.79	[15]
$K_3cit(H_2O)(cr)$	$K_3cit(H_2O)(cr) \leftrightharpoons 3K^+ + cit^{3-} + H_2O$	−1.24	[34]
KH_2citcr	$KH_2cit(cr) \leftrightharpoons K^+ + H_2cit^-$	−6.21	[34]
$Na_3cit(H_2O)_2(cr)$	$Na_3cit(H_2O)_2(cr) \leftrightharpoons 3Na^+ + cit^{3-} + 2H_2O$	−1.19	[34]
$Na_2Hcit(cr)$	$Na_2Hcit(cr) \leftrightharpoons 2Na^+ + Hcit^{2-}$	−3.94	[34]
$NaH_2cit(cr)$	$NaH_2cit(cr) \leftrightharpoons Na^+ + H_2cit^-$	−4.87	[34]

[a] Solubility product was corrected with the Davis equation from $I = 1$ [16].

pastes) under controlled conditions at 20 °C. For experiments with fresh pastes (up to 8 h) the pore solution was collected by vacuum filtration using a 0.45 µm nylon filter. For longer hydration times the pore solution was extracted using the steel die method with pressure up to 250 N/mm^2. The solutions were also filtered through a 0.45 µm nylon filter. One part of the pore solution was then immediately used to measure the pH value. Another part was acidified with HNO_3 supra pure for ICP-OES (and ICP-MS) analysis and diluted 1:10 (1:100 respectively) to prevent the precipitation of solids. A third part was diluted 1:10 using 0.1 M HCl solution to determine the dissolved organic carbon (DOC). The pH-electrode used had been calibrated against KOH solutions with known concentrations (c(KOH) = 0.1–1.0 mol/L) before measurements. The concentrations of Al, Ba, Ca, K, Li, Mo, Na, S, Si and Sr were determined with ICP-OES. Fe and Cr concentrations were determined with ICP-MS.

After the different hydration times, hydration was stopped by immersion of the crushed samples in isopropanol for about 15 min. The samples were then dried at 40 °C, ground by hand to <63 µm and used for XRD and thermogravimetric analyses. XRD analyses were performed on a PANalytical X'Pert Pro using CuKα radiation. For TGA (Mettler Toledo TGA/SDTA851[e]) about 8–12 mg per sample were heated under N_2 over a temperature range of 30 to 980 °C at a rate of 20 °C/min.

Calorimetric measurements were carried out with a Thermometric TAM Air on 6 g of the fresh paste at $w/c = 0.4$.

2.2. Thermodynamic calculations

Thermodynamic calculations were carried out using the geochemical code GEMS-PSI [12]. GEMS-PSI is a broad-purpose geochemical modeling code, which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, gas mixture and aqueous electrolyte are considered simultaneously. The default database of GEMS code was used, which is based on the PSI chemical thermodynamic database [13] expanded with additional data for solids that are expected to form under cementitious conditions [11] as well as with constants for citric acid and some citrate complexes (thermodynamic constants used for citrate are summarized in Table 2).

The geochemical code GEMS-PSI was also used to calculate the saturation indices (SI) for solid phases given by log IAP/K_{S0} (IAP: ion activity product; K_{S0}: solubility product). GEMS was used to calculate based on the measured dissolved concentrations the ion activity product IAP and to compare it to the solubility product of ettringite, gypsum, and portlandite. For these concentrations not only complex formation between the different anorganic species was considered but also complexation by the dissolved citrate.

3. Results and discussion

3.1. Heat evolution rate curves

Heat evolution rate curves allow following the progress of hydration. In the absence of citric acid the main peak of heat release, related mainly to C_3S hydration, was found after approx. 12 h (see Fig. 1). This maximum of heat release was shifted to ~17 h, if 0.1 wt.%

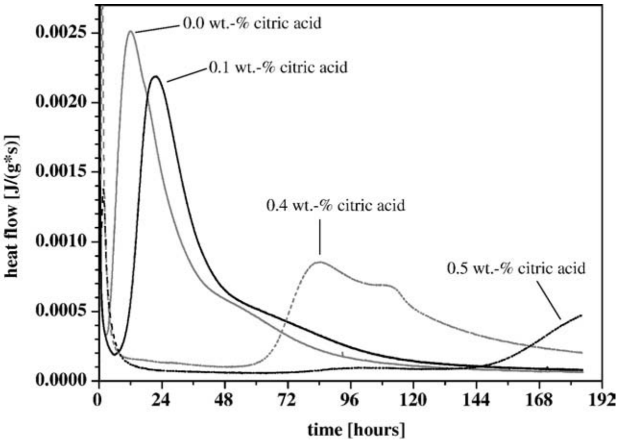

Fig. 1. Heat evolution rate curves of the OPC used (CEM I 42.5 N) with different amounts of added citric acid.

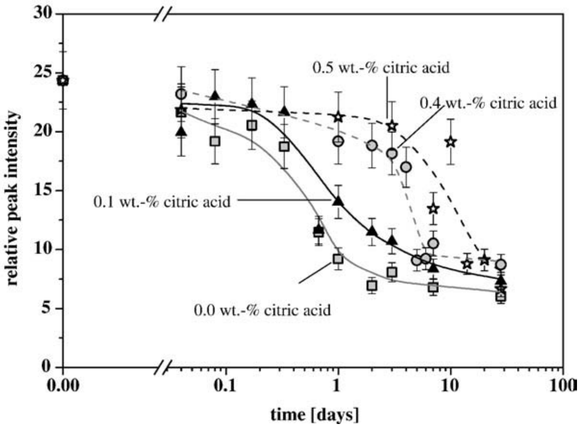

Fig. 2. Changes in the relative peak intensities of the XRD pattern of alite for the samples with and without citric acid at different hydration times. Lines are added to help visualize the data, not as a suggested fit to the data.

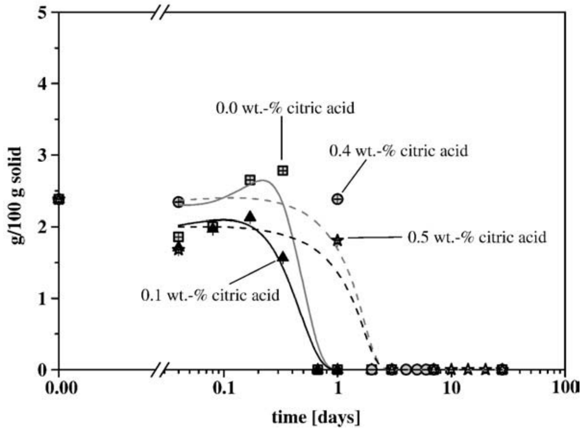

Fig. 4. Gypsum consumption of samples with and without citric acid as a function of hydration time (from TGA measurements). Lines are added to help visualize the data, not as a suggested fit to the data.

citric acid had been added. With 0.4 wt.% citric acid the main peak of heat release occurred only after ~84 h and with 0.5 wt.% citric acid the main peak did not occur before 180 h. With increasing amounts of citric acid the maximum heat release decreased continuously, and the peak broadened, indicating that the addition of citrate strongly retarded the hydration of the used Portland cement. Similarly the total heat release after 180 h decreased from 5.7 J/g to 2.1 J/g in the presence of 0.5 wt.% citric acid. In the presence of 0.1 wt.% citric acid the total heat release amounted to 5.7 J/g like in the plain paste while in the presence of 0.4 wt.% citric acid the amount was 4.7 J/g.

Ramachandran and Lowery [5] observed similar to our observations that the addition of 0.2 wt.% Na-citrate (at a w/c of 0.5) shifted the main peak of heat release from 9 to approximately 20 h. With increasing addition of Na-citrate (up to 0.4 wt.%) the maximum of heat release decreased and the peak broadened. In contrast to these findings Singh et al. [6] found that 0.1 wt.% citric acid accelerated the hydration of Portland cement, while the use of 0.2–0.4 wt.% citric acid retarded the hydration.

3.2. Evolution of solid phases with time

The changes of the composition of the solid phases during hydration were followed by XRD and TGA/DTA. The unhydrated cement contained small quantities of calcite, portlandite and gypsum as observed by TGA measurements. During hydration the quantities of alite, belite, aluminate, and ferrite decreased. The semi-quantative XRD analysis showed that in the absence of citric acid, the amount of alite and aluminate decreased relatively fast, while the amount of belite and ferrite diminished only very slowly. The addition of citric acid to the mixing water showed clearly a retarding effect on the dissolution of the clinker phases and or on the precipitation of hydration products. This is in agreement with the observations by the heat evolution rates (Fig. 1). The XRD analysis showed that upon the addition of citric acid the dissolution of alite slowed down considerably (Fig. 2). For aluminate a much less pronounced retardation in the presence of citric acid was observed (Fig. 3). It is interesting to note that the addition of 0.1 wt.% citric acid seemed to accelerate the hydration of aluminate slightly. This is in a clear contrast to the observation upon the addition of higher dosages of citric acid where a clear retardation was observed (Fig. 3). For belite and ferrite no clear trends could be observed.

In addition, the consumption of gypsum was found to be clearly affected by the presence of citric acid. Thermogravimetric analysis indicated for the samples with 0.0 and 0.1 wt.% citric acid that gypsum is consumed within 16 h. For the samples containing 0.4 and 0.5 wt.% citric acid gypsum still was present after one day (Fig. 4). Also the formation of ettringite slowed down significantly in the presence of citric acid as illustrated in Fig. 5. The retardation of ettringite formation and the retardation in the dissolution of gypsum indicate indirectly a hindrance in the dissolution of aluminate (and/or ferrite). The XRD showed that after 3 and 7 days, the amount of ettringite was higher for the samples prepared with 0.4 and 0.5 wt.% citric acid than for the samples with 0.0 and 0.1 wt.% citric acid (Fig. 5). For TGA measurements, however, no such

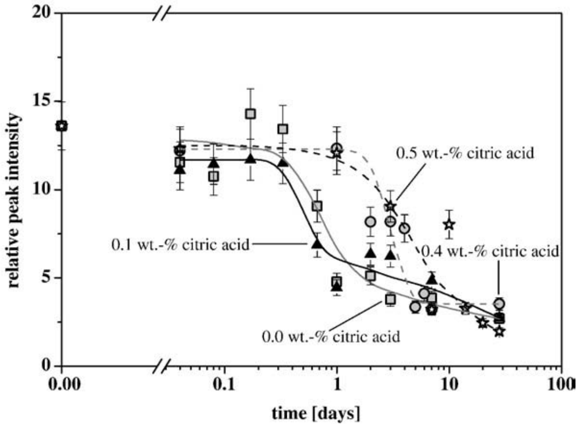

Fig. 3. Changes in the relative peak intensities of the XRD pattern of aluminate for the samples with and without citric acid at different hydration times. Lines are added to help visualize the data, not as a suggested fit to the data.

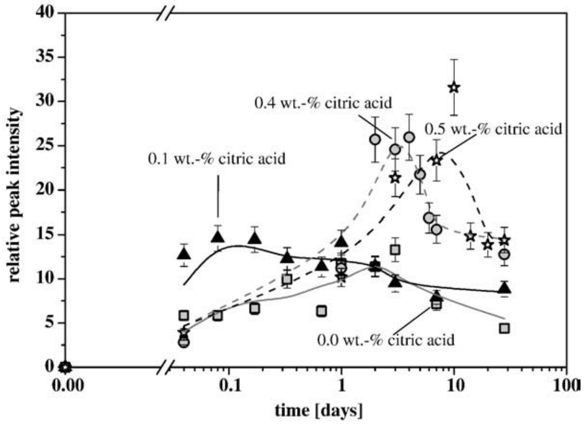

Fig. 5. Changes in ettringite content of samples with and without citric acid as a function of hydration time based on the semi-quantitative evaluation of the XRD pattern. Lines are added to help visualize the data, not as a suggested fit to the data.

effect was evident. Similar to our findings, Rottstegge et al. [14] observed by solid state NMR also the formation of more ettringite in the presence of citric acid. Despite the fact that the ettringite formation slowed down in the samples containing 0.4 and 0.5% citric acid, the formation of ettringite during the first hour of hydration was accelerated in the sample containing 0.1% compared to the sample without citric acid. Figs. 3 and 4 show that after one hour of hydration the consumption of aluminate and gypsum was slightly higher for the sample with 0.1% citric acid than for the sample without citric acid. Hence, after one hour of hydration the sample with 0.1% citric acid contained more ettrinigte than the sample without citric acid (cf. Fig. 5) which agrees with TGA measurements.

The amount of calcite declined slightly in all samples during hydration. No significant differences in the presence of the various concentrations of citric acid could be observed. The amount of portlandite increased strongly during hydration in samples with and without citric acid. The formation of portlandite was retarded significantly by the addition of citric acid (Fig. 6). In the presence of 0.5 wt.% of citric acid, only after more than 20 days a similar amount of portlandite was formed as in the absence of citric acid. Also the formation of C–S–H was retarded in the presence of citric acid as illustrated in Fig. 7. The observed slow down of portlandite and C–S–H formation is consistent with the retardation in the dissolution of C_3S and possibly also of C_2S (Fig. 7B). After 28 days the amount of C_3S and C_2S was similar in all samples indicating that also a similar amount of C–S–H-phases was present in all samples (Fig. 7B).

The findings seemed to indicate that C_3S hydration is delayed by the addition of citric acid but that C_3A hydration and/or the formation of ettringite can be accelerated in the presence of small amounts of citrate. This effect could have been the cause for the acceleration of hydration observed by Singh et al. [6] upon the addition of 0.1 wt.% citric acid as they used an OPC which contained 11% C_3A. Higher addition of citrate led clearly also to retardation of C_3A hydration. Whether also the dissolution of C_2S and C_4AF was affected by the presence of citric acid could not be verified as the semi-quantative XRD analysis showed no significant differences for these two phases.

Our observations agree with Rottstegge et al. [14] who reported a retardation of the dissolution of C_3S. In addition, these authors found, by solid state NMR that the C_3A dissolution altered. In contrast to our finding, Schwarz [7] postulated an accelerated hydration of ferrite in the presence of citrate, which could not be confirmed in the title study.

3.3. Changes in the pore solution

Citrate forms complexes with a number of cations, such as Ca^{2+}, Al^{3+} or Fe^{3+}. Complexes of citrate with three-valent cations such as Al^{3+} or Fe^{3+} are generally more stable than complexes with bivalent of monovalent cations [15,16]. Such a complexation of the cations present in the pore solution could lead to a retardation of the formation of hydrates. Thus, the composition of the liquid phase was investigated in the presence and absence of citric acid.

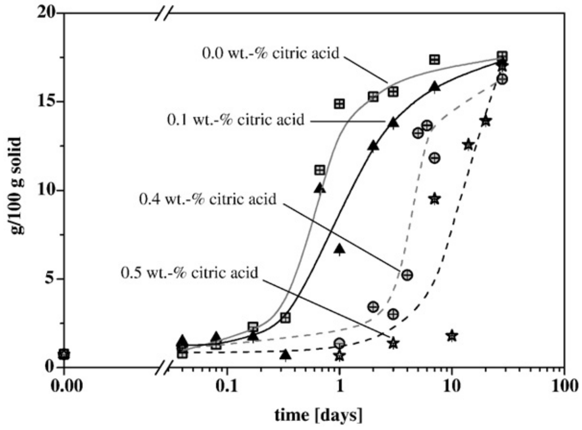

Fig. 6. Portlandite content of samples with and without citric acid as a function of hydration time (from TGA measurements). Lines are added to help visualize the data, not as a suggested fit to the data.

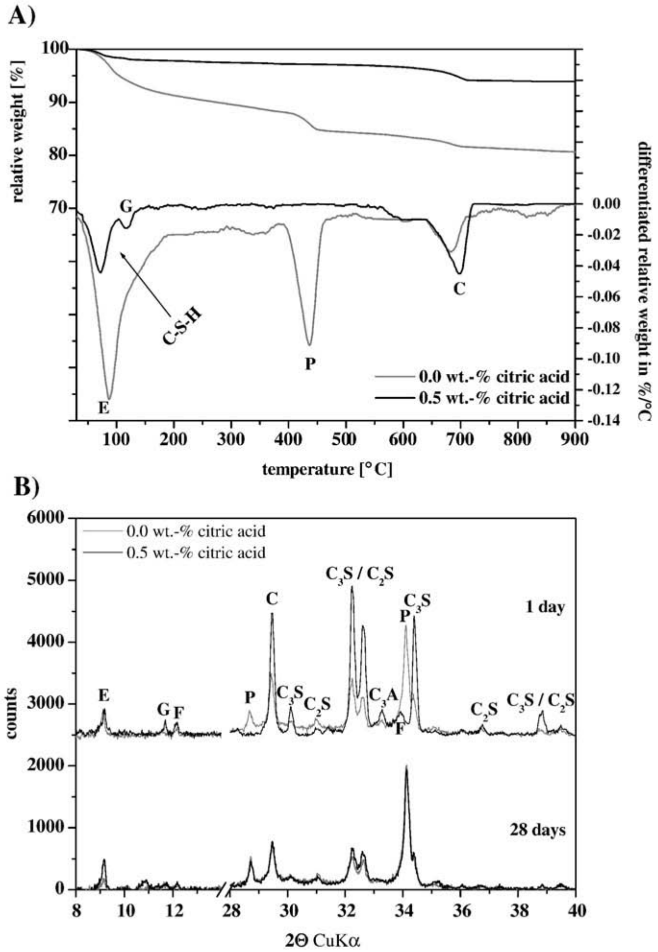

Fig. 7. Thermogravimetric (A) and XRD (B) analyses for the samples without and 0.5 wt.% citric acid after one day (28 days respectively) of hydration. E: ettringite; G: gypsum; F: ferrite; P: portlandite; C: calcite.

In the absence of citric acid, the composition of the pore solution was dominated by K, sulfate, hydroxide, Na and Ca (Table 3) during the first day. The high concentrations of K, Na and sulfate were due to the fast dissolution of alkali-sulfate phases. K and Na increased constantly during hydration time as i) the amount of pore solution present decreases with time as the water is consumed by the different hydration products and as ii) the alkalis present in the clinker phases (cf. Table 1) were released slowly. In the absence of citric acid the concentrations of Ca, sulfate, and hydroxide stayed relatively constant during the first day as their concentrations in the pore solution were limited by the presence of gypsum and portlandite (cf. Figs. 4 and 6). The disappearance of gypsum after approximately one day led to an abrupt decrease of the concentrations of Ca and S and to a strong increase in pH (Table 3). The concentrations of Al, Fe, and Si were very low during the first day of hydration and showed a slight decrease during the first 16 h. After one day, however, as pH increased also the concentrations of Al, Fe, and Si increased (cf. Table 3).

In the presence of 0.1 wt.% citric acid the composition of the pore solution did not differ much from the composition of the pore solution in the absence of citric acid. Only the concentrations of potassium were considerably lower in the presence of 0.1 wt.% citric acid than in the absence of citric acid. In average, 40 mmol less K were present in

Table 3
Composition of the pore solution after different hydration times. The measured concentrations have standard deviations of approximately ±10%.

Time in days	K	Na	Ca	Fe	Al	Si	S	OH^-	DOC
	mmol/l								
No citric acid									
0.04	392	25	16	0.249	0.011	0.12	151	120	22
0.08	361	23	21	0.142	0.007	0.13	131	140	11
0.2	365	23	23	0.036	<0.004	0.10	123	160	10
0.3	488	33	10	0.027	0.005	0.08	177	180	10
0.7	385	30	19	0.003	<0.004	0.08	147	140	18
1	410	34	9.5	0.004	0.006	0.10	122	190	4.1
2	437	37	3.0	0.009	0.028	0.17	36	390	4.2
3	474	42	2.3	0.018	0.074	0.21	10	430	4.6
7	531	49	1.8	0.02	0.130	0.21	8.0	540	5.3
28	626	62	1.6	0.064	0.137	0.25	15	600	7.2
0.1% citric acid									
0.04	341	23	18	0.086	0.010	0.16	138	110	15
0.08	350	23	19	0.063	0.012	0.13	135	130	13
0.2	362	24	22	0.050	0.004	0.10	129	150	13
0.3	349	23	23	0.024	0.009	0.09	118	160	13
0.7	355	24	20	0.006	0.005	0.06	125	140	8.2
1	372	29	17	<0.003	0.005	0.08	136	160	3.0
2	417	35	3.4	<0.003	0.018	0.16	36	380	4.3
3	449	39	2.3	<0.003	0.063	0.20	8.2	400	3.8
7	494	45	1.8	<0.003	0.122	0.20	6.8	520	3.7
28	574	56	1.7	<0.003	0.133	0.23	12	560	7.2
0.4% citric acid									
0.04	281	28	47	0.394	<0.004	0.04	147	64	61
1	332	36	25	0.018	<0.004	0.04	115	190	21
2	377	26	19	0.006	0.006	0.07	109	200	14
3	384	27	20	0.005	<0.004	0.08	122	190	13
4	357	25	17	<0.003	0.005	0.07	113	190	9.2
5	411	34	2.9	<0.003	0.103	0.19	1.6	410	2.5
6	430	35	2.8	<0.003	0.097	0.22	1.8	410	3.2
7	424	37	2.3	<0.003	0.158	0.20	1.5	450	8.3
28	534	53	1.6	<0.003	0.221	0.27	5.0	530	10
0.5% citric acid									
0.04	281	29	50	1.1	<0.004	0.07	147	66	63
1	289	19	40	0.168	0.007	0.09	142	77	45
3	327	21	25	0.046	0.005	0.04	101	180	27
7	363	24	25	0.014	0.004	0.06	110	200	18
10	402	29	16	0.028	<0.004	0.08	101	230	16
14	427	38	2.8	0.008	0.129	0.22	<1.6	410	3.9
20	448	42	2.6	0.012	0.127	0.21	1.9	380	5.1
28	574	57	1.7	0.014	0.250	0.26	4.9	530	7.6

the absence of citrate than in the present of 0.1 wt.% of citric acid (corresponding to 13 mmol/l citrate). A possible explanation for this decrease of K concentration could be that the potassium could act as a counterion for citrate $C_6H_5O_7^{3-}$ which has been sorbed or precipitated as K-citrate. The K concentrations of the samples containing 0.4 and 0.5% of citric acid (corresponding to 52 and 65 mmol/l) were after 1 h approximately 110 mmol/l lower than in the absence of citrate (cf. Table 3). These observations are again consistent with the idea that a significant part of the negative charge of citrate which either precipitated or sorbed on the solids present, is compensated by K. In contrast to K, the concentrations of Na were not significantly affected by the presence of citrate. Singh et al. [6] observed similarly a strong decrease of dissolved K concentration by approximately 60 mmol/l upon the addition of 20 mmol/l citric acid.

For the samples with 0.4 and 0.5 wt.% citric acid the strong retardation effect of citric acid could be seen in the composition of the pore solution even more clearly than in the results of XRD and TGA. The sharp decrease of Ca and sulfate in the pore solution happened for the samples containing 0.4 wt.% citric acid not until four days of hydration, and after 10 days in the samples containing 0.5 wt.% citric acid. Also the corresponding increase of hydroxide, Al and Si concentrations could be observed at these hydration times (cf. Table 3). This strong retardation agreed with the later consumption of gypsum in the presence of citric acid as observed by TGA and XRD analyses (Fig. 4) and the retardation of the dissolution of aluminate (Fig. 3).In addition the dissolution of alite also slowed down.

During the first day the pore solutions were oversaturated in all samples with respect to gypsum, portlandite and ettringite (Fig. 8). The saturation indices SI, given by log IAP/K_{S0} (IAP: ion activity product; K_{S0}: solubility product), of gypsum, portlandite and ettringite were >0, indicating that thermodynamic equilibrium had not yet been reached. In absence of citric acid, after one day the calculated SI of

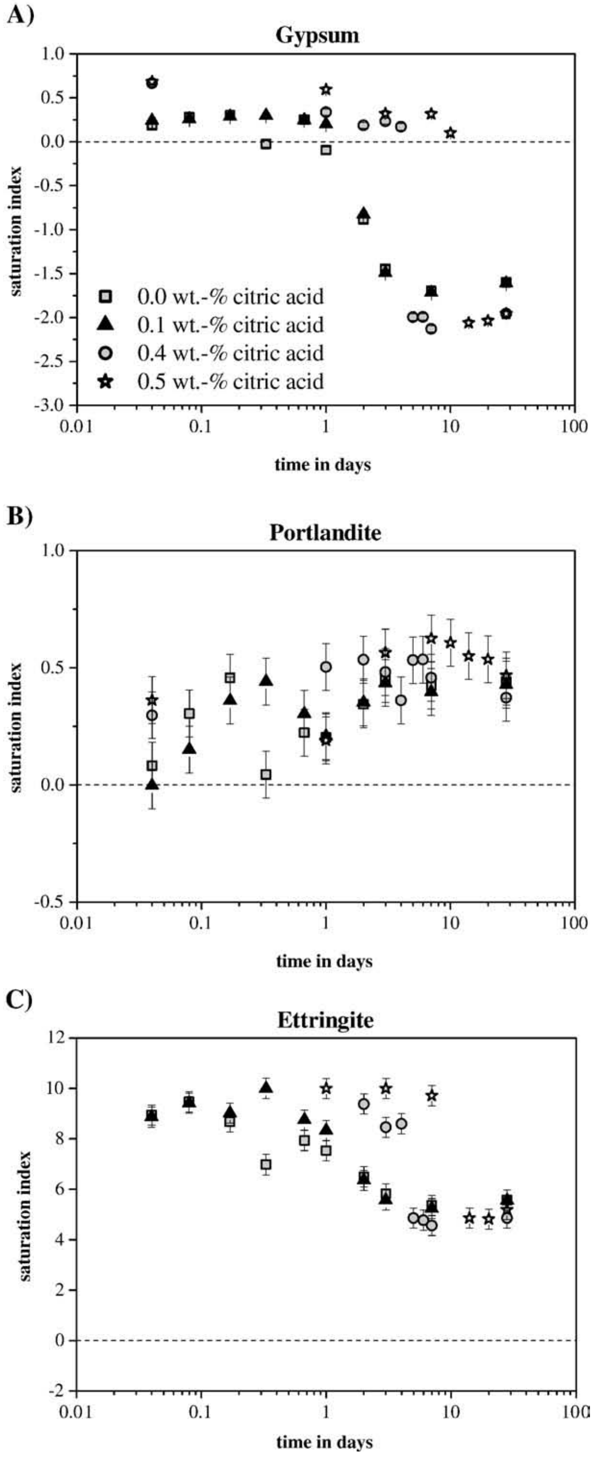

Fig. 8. Saturation indices of gypsum (A), portlandite (B), and ettringite (C) calculated as a function of hydration time. A saturation index of 0 indicates equilibrium between liquid and solid phase. Note: Error bars for the SI of gypsum (A) are smaller than the symbols.

gypsum dropped to <0, indicating the complete dissolution of gypsum. This observation agreed well with TGA measurements, where no gypsum was detected for the sample without citric acid after one day of hydration (Fig. 4). The retarded consumption of gypsum in the presence of citric acid (cf. Section 3.2.) is also mirrored in the saturation factors: for 0.1 wt.% citric acid SI was <0 after 2 days, for 0.4 wt.% citric acid after 5 days, and for 0.5 wt.% citric acid SI was <0 only after 14 days (Fig. 8A). While the calculated saturation factors after one hour of hydration for the samples containing 0.0 and 0.1% citric acid are similar the calculated saturation factors for the samples containing 0.4 and 0.5% citric acid were somewhat higher (Fig. 8A). The used Portland cement contained small quantities of β calcium hemihydrate ($CaSO_4 \cdot 0.5H_2O$). Previous studies showed that citric acid retards the transformation of β calcium hemihydrate into gypsum [17,18]. Thus, the slightly higher calculated saturation indices for gypsum for the samples containing 0.4 and 0.5% citric acid could be an indication for the retarded transformation of β calcium hemihydrate into gypsum during the first hour of hydration.

Even though the degree of oversaturation of ettringite dropped upon the consumption of gypsum, the solution remained oversaturated with respect to ettringite as well as with respect to portlandite. A similar oversaturation for ettringite and portlandite was also observed in previous studies [19–23] and the calculated saturation indices were partly similar to this study [20,21]. The source of the oversaturation with respect to ettringite or portlandite is unknown [19,20]. In synthetic solutions (i.e. in pure systems containing aluminum, calcium, alkalis, sulfate, and hydroxide) equilibrium, saturation respectively, is reached within a few days [24]. One possible explanation could be that the used high pressures in order to obtain the pore solutions from the hardened cement pastes could cause changes in the pore solution. But also kinetic barriers like high ionic strength could be an explanation for the oversaturation with respect to ettringite and portlandite [19].

The calculated saturation factors for portlandite can be related to the cement hydration over time. The maximum of portlandite oversaturation corresponds to the acceleration period and thus to the dissolution of alite [25]. Maximum portlandite oversaturation was observed for the sample without citric acid after 4 h of hydration, for the sample with 0.1% citric acid after 8 h, for the sample containing 0.4% citric acid after 2 days of hydration, and for the sample containing 0.5% citric acid after 7 days of hydration. This corresponds well with the observed acceleration periods measured by heat evolution measurements (Fig. 1).

3.3.1. Fate of citrate

The amount of dissolved citrate, $C_6H_5O_7^{3-}$, was measured as dissolved organic carbon (DOC). The measured DOC concentrations (6 mmol of DOC correspond to 1 mmol of citrate) are reproduced in Fig. 9 A and Table 3. The measured concentrations showed that citric acid was quickly removed from pore solution. After one hour already up to 90% of the citric acid added has been removed from the pore solution and with increasing hydration times the removal increased up to nearly 100% independent from the initial concentration of citric acid. A similar fast and high removal of citric acid from the pore solution was also found by Smillie and Glasser [8]. They observed the complete removal of citric acid within the first two hours when 2.6 mmol/l citric acid have been added. At higher concentrations (15.6 mmol/l) citric acid has been removed from the pore solution after 14 h [8].

Since the citric acid added is basically removed from the solution within the first hours, it can be expected that only a small fraction of the cations (K, Ca, Na,…) present in the solution is complexed by citrate. This agrees with the experimental data as presented in Table 3 where no significant increase of Na, K, Al or Fe concentration was observed. Only Ca concentrations were increased in the presence of higher concentrations of citrate in solution (Fig. 9B).

Citrate can form mononuclear tridentate surface complexes with metal oxides (e.g. [26–28]). The formation of bi- or multidentate mononuclear surface complexes increases the dissolution rate of solids, especially at low and neutral pH. Pokrovsky et al. [26] and Gobulev and Pokrovsky [28] observed at pH 7.6 and 6 an acceleration of brucite ($Mg(OH)_2$) and diopside ($CaMgSi_2O_6$) dissolution in the presence of citrate. At pH 10.5, however, no increase of diopside dissolution was observed in the presence of citrate. Ahmed and Youssof [29] observed that the dissolution rate of soda–lime–silica glass decreased upon the addition of citrate ($c(\text{citrate}) = 33.0$ mM corresponding to a pH-value of 2.2). They attributed it to the formation of citrate-containing solids on the surface of the glass then acting as an effective barrier against the further dissolution of the glass. Teng and Grandstaff [30] also observed that in the presence of citric acid the dissolution of basaltic glass decreases at pH ≥ 7 and they also observed that secondary phases are formed, but contrary to Ahmed and Youssof [29], Teng and Grandstaff [30] did not state that citrate is incorporated into these secondary phases. Even though the mechanisms of the decrease of the glass dissolution are not fully understood, the formation of such complexes on the surface of the hydrating clinkers could be a possible explanation for the observed decrease of the dissolution rate at high pH-values.

3.3.2. Thermodynamic calculations

Previous studies state that the hydration of cements in the presence of citric acid is retarded because citrate in the pore solution forms stable complexes with cations [9] or because citrate is adsorbed

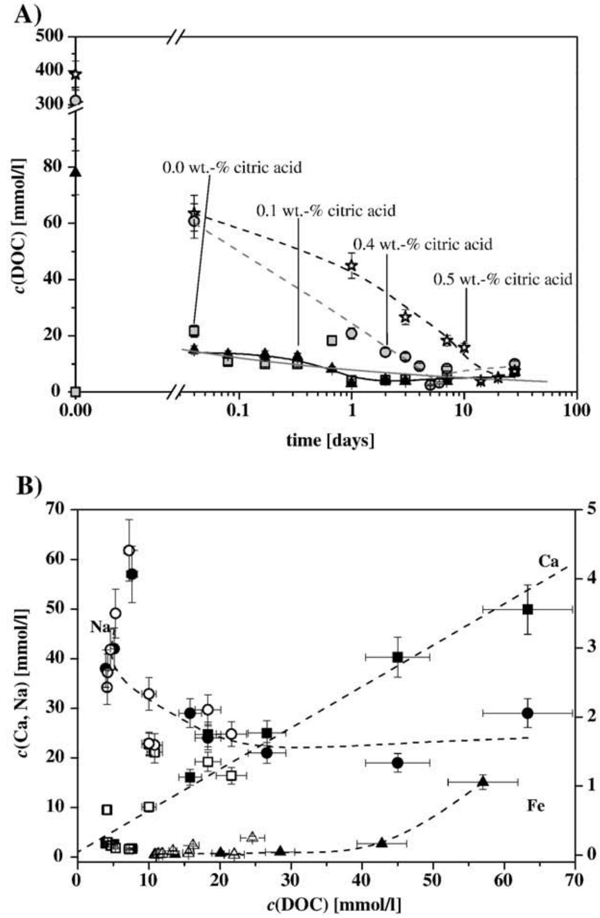

Fig. 9. A) Concentration of the dissolved organic carbon (DOC) of samples with and without citric acid as a function of hydration time and B) measured concentrations of Ca, Na, Fe, and C in presence of 0.5 wt.% citric acid (filled symbols) and in the absence of citric acid (empty symbols). Note: 6 mmol of DOC correspond to 1 mmol of citrate. Lines are added to help visualize the data, not as a suggested fit to the data.

Table 4
Calculated concentrations of complexes of the different cations with citrate for the samples with 0.5 wt.% citric acid. Retardation of cement hydration was not considered.

	Days				
	0.04	1	3	7	28
Measured citrate in mmol/l	10.5	7.5	4.4	3.1	1.3
Calculated percentage of citrate complexes					
	%				
$Cacit^-$	9.0	1.0	0.2	0.2	0.1
$Kcit^{2-}$	0.03	0.03	0.04	0.03	0.03
$Nacit^{2-}$	0.002	0.004	0.006	0.006	0.006
$AlcitOH^-$	<0.001	<0.001	<0.001	<0.001	<0.001
$Fe(III)citOH^-$	<0.001	<0.001	<0.001	<0.001	<0.001
cit^{3-}	90.9	99.0	99.7	99.8	99.8
Total citrate	100	100	100	100	100
Calculated total citrate in mmol/l	10.5	7.5	4.5	3.0	1.2
Measured ion concentrations and calculated complex concentrations in pore solution					
	mmol/l				
$Ca_{\text{total, measured}}$	50	40	25	25	1.7
$Cacit^-{}_{\text{calculated}}$	0.95	0.08	0.009	0.006	0.001
	%				
$Ca_{\text{dissolved, calculated}}$	98.11	99.81	99.96	99.98	99.92
	mmol/l				
$K_{\text{total, measured}}$	281	289	327	363	574
$Kcit^{2-}{}_{\text{calculated}}$	0.0032	0.0023	0.0018	0.0009	0.0004
	%				
$K_{\text{dissolved, calculated}}$	99.999	99.999	100	100	100

onto the positively charged surface of the Portland cement grains [6]. In order to examine the extent of the supposed formation of cation–citrate-complexes thermodynamic calculations were carried out using complex formation constants of citrate as compiled in Table 2.

Thermodynamic calculations showed that in the presence of e.g. 10.5 mmol/l citrate (as measured after 1 h of hydration for the sample containing 65 mmol/l citric acid) 9% of the total citrate in solution was expected to be present as $Cacit^-$ ($CaC_6H_5O_7^-$) complexes (Table 4). This means that less than 2% of the measured Ca ($c(\text{Ca}) = 50$ mmol/l, Tables 3 and 4) was complexed by citrate after 1 h. With proceeding hydration the percentage of complexed Ca even decreased (Table 4). The fraction of K and Na complexed by citrate was even smaller. Considerably less than 1% of the total dissolved citrate was calculated to form complexes with K and Na. The calculated complexation of Al and Fe by citrate was <0.001% due to the very low concentrations of both elements present in the pore solution (Table 3). Fig. 9B shows the correlation between Ca, Na, Fe, and dissolved organic carbon (C). Ca and C show a linear correlation for the sample in the presence with 0.5 wt.% citric acid. However, the conducted thermodynamic calculations showed that the formation of cation–citrate-complexes is very limited. This is in accordance to the measured cation concentrations in the pore solutions where no significant differences and no significant trends were observed between the samples in presence and absence of citric acid (Table 3), with exception of the strong decrease of K concentrations (see below).

Based on the experimental observations and on the thermodynamic calculations, the addition of citric acid led after one hour or longer to a very limited complexation of aqueous ions by citrate due to the quick removal of citric acid from the pore solution. This makes retardation of the precipitation of the hydrates by complex formation improbable.

However, thermodynamic calculations could not prove that crystalline K-citrate was formed the measured potassium and citrate concentrations were much lower than the reported ion concentrations for the solubility product of K-citrate (cf. Table 2). The measured K concentrations, however, decreased strongly in the samples where citric acid has been added. It should be noted that on a molar basis approximately 3 times more K “disappear” from the pore solution than citrate ($C_6H_5O_7^{3-}$) both in our experiments as well as in the experiments of Singh et al. [6]. This molar ratio of 3 between K and citrate could indicate that K is used to counterbalance the negative charge of sorbed (or precipitated) citrate. Thus, the observed strong retardation could be caused by a blocking of the surface of the clinker grains by sorption of (K-)citrate on their surface.

4. Conclusions

Observations of the solid phases showed that the dissolution of alite and aluminate slowed down considerably in the presence of citric acid and therefore, also the formation of the different hydration products. Analyses of the dissolved organic carbon showed that citric acid was removed almost quantitatively from the pore solution after the first hours of cement hydration.

The compositions of the pore solutions did not differ much. Only for calcium a moderate correlation between measured concentrations of citrate and Ca could be found. The addition of citric acid decreased the potassium concentrations in pore solution, indicating that K acts as a counter ion of the negatively charged citrate ($C_6H_5O_7^{3-}$) on the surface of the Portland cement clinker grains.

Thermodynamic calculations could confirm that the complexation of ions by citrate is very limited in cementitious systems and thus, could not be the retarding mechanism.

The observed retarded dissolution of alite and aluminate and the mainly unchanged composition of the pore solution as well as the fast removal of citrate from the pore solution argue for the precipitation or sorption of citrate onto the surface of the clinker grains. However, thermodynamic calculations could not confirm that a crystalline citrate species precipitated. Hence, it is suggested that (potassium-) citrate was sorbed onto the clinker grain surface and formed a protective layer around the clinker grains and thus, retarded the dissolution of the clinker phases.

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References

[1] J. Tinnea, J.F. Young, Influence of citric acid on reactions in the system $3CaO \cdot Al_2O_3$–$CaSO_42H_2O$–CaO–H_2O, J. Am. Ceram. Soc. 60 (9–10) (1977) 387–389.

[2] N.B. Singh, A.K. Singh, S. Prabha Singh, Hydration study of the system $Ca_3Al_2O_6$–$CaSO_42H_2O$–$Ca(OH)_2$–H_2O with and without citric acid, J. Am. Ceram. Soc. 73 (10) (1990) 3063–3068.

[3] C. Stadelmann, Zur Wirkung von Citronensäure auf die Hydratation von Tricalciumsilicat (Ca_3SiO_5), Z. Anorg. Allg. Chem. 547 (1987) 127–132.

[4] C.R. Wilding, A. Walter, D.D. Double, A classification of inorganic and organic admixtures by conduction calorimetry, Cem. Concr. Res. 14 (2) (1984) 185–194.

[5] V.S. Ramachandran, M.S. Lowery, Conduction calorimetric investigation of the effect of retarders on the hydration of Portland cement, Thermochim. Acta 195 (1992) 373–387.

[6] N.B. Singh, A.K. Singh, S. Prabha Singh, Effect of citric acid on the hydration of Portland cement, Cem. Concr. Res. 16 (6) (1986) 911–920.

[7] W. Schwarz, Novel cement matrices by accelerated hydration of the ferrite phase in Portland cement via chemical activation: kinetics and cementitious properties, Adv. Cem. Based Mater. 2 (1995) 189–200.

[8] S. Smillie, F.P. Glasser, Reaction of EDTA, oxalic acid and citric acid with Portland cement, Adv. Cem. Res. 11 (2) (1999) 97–101.

[9] W. Schwarz, K. Sujata, H.M. Jennings, A. Gerdes, H. Sadouki, F.H. Wittmann, Chemically modified hydration of Portland cement, AEDIFICATIO Publishers, Freiburg i. Br., 1994

[10] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement, Cem. Concr. Res. 36 (2) (2006) 209–226.

[11] B. Lothenbach, T. Matschei, G. Möschner, F.P. Glasser, Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement, Cem. Concr. Res. 38 (1) (2008) 1–18.

[12] D.A. Kulik, GEMS-PSI 2.12, PSI Villigen, Switzerland; available at http://les.web.psi.ch/Software/GEMS-PSI/index.html.

[13] W. Hummel, U. Berner, E. Curti, F.J. Pearson, T. Thoenen, Nagra/PSI Chemical Thermodyanmic Data Base 01/01, Universal Publishers/uPublish.com, Parkland, Florida, 2002.

[14] J. Rottstegge, M. Wilhelm, H.W. Spiess, Solid state NMR investigations on the role of organic admixtures on the hydration of cement pastes, Cem. Concr. Compos. 28 (2006) 417–426.

[15] NEA - Nuclear Energy Agency, Thermochemical Database Project (TDB), 2006, http://www.nea.fr/html/dbtdb/.

[16] L.-C. Königsberger, E. Königsberger, P.M. May, G.T. Hefter, Complexation of iron (III) and irong (II) by citrate. Implications for iron speciation in blood plasma, J. Inorg. Biochem. 78 (2000) 175–184.

[17] A. Ersen, A. Smith, T. Chotard, Effect of malic and citric acid on the crystallisation of gypsum investigated by coupled acoustic emission and electrical conductivity techniques, J. Mater. Sci. 41 (2006) 7210–7217.

[18] J.-R. Hill, J. Plank, Retardation of setting of plaster of Paris by organic acids: understanding the mechanism through molecular modeling, J. Comput. Chem. 25 (12) (2004) 1438–1448.

[19] B. Lothenbach, G. Le Saout, E. Gallucci, K. Scrivener, Influence of limestone on the hydration of Portland cements, Cem. Concr. Res. 38 (6) (2008) 848–860.

[20] D. Rothstein, J.J. Thomas, B.J. Christensen, H.M. Jennings, Solubility behaviour of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of hydration time, Cem. Concr. Res. 32 (10) (2002) 1663–1671.

[21] J. Stark, B. Möser, F. Bellmann, C. Rössler, Thermodynamische Modellierung der Hydratation von OPC, in: Q.C.D. Zementhydratation (Ed.), Proc 16. Internationale Baustofftagung (ibausil), Weimar, Germany, 20, September 2006, 1-0047 – 1-0066, -22.

[22] S. Goni, M.P. Lorenzo, M.S. Hernández, Calcium hydroxide saturation factors in the pore solution of hydrated Portland cement fly ash pastes, J. Am. Ceram. Soc. 79 (4) (1996) 1041–1046.

[23] E.M. Gartner, F.J. Tang, S.J. Weiss, Saturation factors for calcium hydroxide and calcium sulfates in fresh Portland cement pastes, J. Am. Ceram. Soc. 68 (12) (1985) 667–673.

[24] R.B. Perkins, C.D. Palmer, Solubility of ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O$) at 5–75 °C, Geochim. Cosmochim. Acta 63 (13/14) (1999) 1969–1980.

[25] S. Garrault-Gauffinet, A. Nonat, Experimental investigation of calcium silicate hydrate (C–S–H) nucleation, J. Cryst. Growth. 200 (1999) 565–574.

[26] O.S. Pokrovsky, J. Schott, A. Castillo, Kinetics of brucite dissolution at 25 °C in the presence of organic and inorganic ligands and divalent metals, Geochim. Cosmochim. Acta 69 (4) (2005) 905–918.

[27] S.V. Golubev, A. Bauer, O.S. Pokrovsky, Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 °C, Geochim. Cosmochim. Acta 70 (2006) 4436–4451.

[28] S.V. Golubev, O.S. Pokrovsky, Experimental study of the effect of organic ligands on diopside dissolution kinetics, Chem. Geol. 235 (2006) 377–389.

[29] A.A. Ahmed, I.M. Youssof, Attack on soda–lime–silica glass bottles by acetic, citric and oxalic acids, Glass Sci. Technol. 70 (3) (1997) 76–85.

[30] H. Teng, D.E. Grandstaff, Dissolution of basaltic glass: effects of pH and organic ligands, Eur. Mater. Res. Soc. 412 (1996) 249–256 (Symposium Proceedings).

[31] H.W.F. Taylor, Cement Chemistry, Thomas Telford Publishing, London, 1997.

[32] T.E. Zelenina, O.Y. Zelenin, Complexation of citric and tartaric acids with Na and K ions in aqueous solution, Russ. J. Coord. Chem. 31 (4) (2005) 235–242.

[33] R.B. Martin, Citrate binding of Al^{3+} and Fe^{3+}, J. Inorg. Biochem. 28 (1986) 181–187.

[34] A. Apelblat, Enthalpies of solution of citrates and hydrogen citrates of lithium, sodium, and potassium, J. Chem. Thermodyn. 26 (1994) 49–51.