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THERMAL STUDIES OF THE HARDENING OF THE SYSTEMS CALCIUM SILICATES–ELECTROLYTE–WATER

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Abstract

Thermal studies, sometimes together with X-ray analysis, were applied to investigate the process of hydration in the systems calcium silicates (tricalcium silicate or dicalcium silicate) – water – electrolyte. Alkali metal or alkaline–earth metal salts were used as electrolytes. Results and conclusions are presented concerning the action of electrolytes upon the kinetics of hardening of the calcium silicates and the composition and phase transformation of calcium hydrosilicate in the presence of low proportions of electrolytes (0.5, 2 and 5 mass%), these effects being due to ionic substitution. A higher proportion of electrolyte (above 2%) in the systems calcium silicate –water can determine the formation of a complex salt, e.g. calcium hydroxysalts or double hydrosilicates.

Keywords: calcium silicate, calcium silicate hydration, electrolyte admixtures, thermal studies of hydration

Introduction

The calcium silicates play a fundamental role in inorganic binder systems. The hardening process in such systems is essentially controlled by the chemical reactions, which take place and consequently by the factors which influence these reactions and by the ability of the calcium hydrosilicates to develop a polycondensation-crystallization hardened structure. For control of the hardening process, an important role is played by the adequate choice of additives, e.g. electrolytes, which exhibit a high degree of dissociation [1–13]. As the hardening process is very complex, its investigation necessitates the use of various experimental methods with a high-resolution capacity. Thermal analysis is such a method. It can provide adequate information and can substitute other methods of investigation.

In the present paper, the systems calcium silicate binder (C_3S or β-C_2S^*) water – electrolytes have been investigated. As electrolyte, alkali metal and alkaline–earth metal salts were used.

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* C=CaO; S=SiO$_2$ and H=H$_2$O

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Experimental

The calcium silicates (C_3S and β-C_2S) were synthesized by solid-state reactions from chemically pure reagents ($CaCO_3$ and SiO_2) in stoichiometric ratio. The corresponding mixtures were burnt three or four times at 1450–1500°C for 3 to 4 h, in an electric furnace [3]. As electrolytes alkali metal chlorides (LiCl, NaCl or KCl), alkaline-earth metal chlorides ($CaCl_2$, $SrCl_2$ or $BaCl_2$) and inorganic calcium salts such as $CaCO_3$, $CaSO_4$ and $Ca(NO_3)_2$ were used. The admixtures comprised 0.5, 2.0 and 5.0% by mass of the binder. In this way, the influence of the cation can be followed with a given anion, and the influence of the anion can be studied when the cation is the same. The chemical bound water, the hydration degree and the ratios CaO/SiO_2 and H_2O/SiO_2 were determined for the calcium silicate systems after various hardening periods, using DTA (on 500 mg powder with particle dimensions ≤63 μm, between 25 and 1000°C, at a heating rate of 10°C min^{-1}, and X-ray analyses (powder with particle dimensions ≤ 0.63 μm with CuK_α radiation and 2θ=8–80°).

Results

Figures 1 and 2 show as examples DTA curves corresponding to hardened pastes of C_3S and β-C_2S with and without electrolytes. Tables 1 and 2 list the characteristic thermal effects. The following categories of thermal effects can be identified:

- the range 115–170 (190)°C corresponding to calcium hydrosilicates dehydration, and particularly to the loss of gel water;

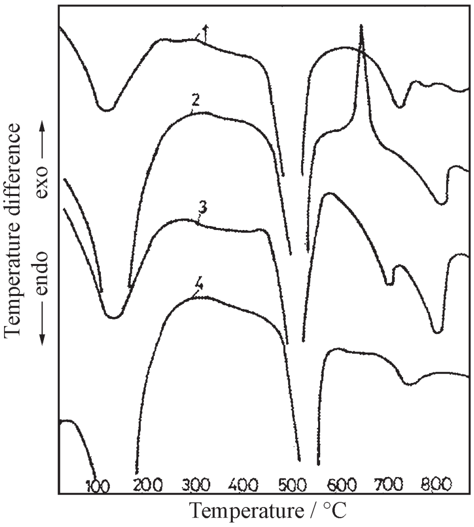

Fig. 1a DTA pattern of C_3S after hardening for 28 days without electrolyte (1) or with 2% LiCl (2), 2% NaCl (3) or 2% KCl (4)

- the range 470–535°C, in which the effects are attributed to the calcium hydroxide dehydration. This is more significant in the C_3S system than in the β-C_2S system, because, primarily an important quantity of $Ca(H_2O)$ is released during the hardening process;
- the range above 700°C relates to endothermic effects characteristic of complete dehydration of the calcium hydrosilicate and, eventually, calcium carbonate decomposition. $CaCO_3$ results from the reaction with atmospheric CO_2.

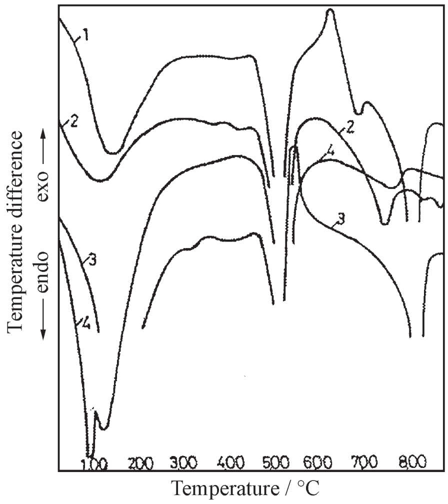

Fig. 1b DTA pattern of the systems C_3S-electrolyte after hardening for 28 days: 2% $CaCl_2$ (1), 0.5% $CaCl_2$ (2), 5% $CaCl_2$ (3) or 2% $Ca(NO_3)_2$ (4)

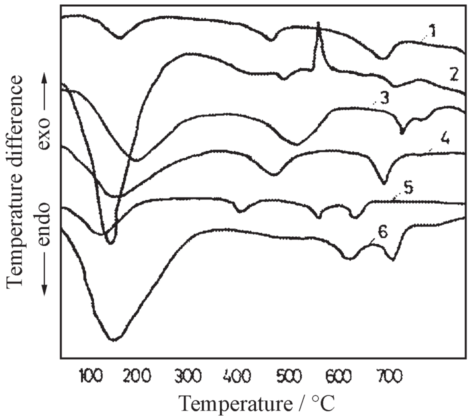

Fig. 2 DTA pattern of β-C_2S after hardening for 28 days without electrolyte (1) or with 2% LiCl (2), 2% NaCl (3), 2% KCl (4), 2% $CaCl_2$ (5) or 2% $Ca(NO_3)_2$ (6)

Table 1 Thermal effects in DTA analyses of hydrated $3CaO\cdot SiO_2$ samples

Electrolyte/%		Hydration time/ days	Temperature interval/°C				
			115–165	510–545	560–660	700–785	805–890
	0	1	– 115*	– 535	–	– 765	– 810
		7	– 125	– 520	–	–	–815; –830
		28	– 150	– 520	–	– 755	– 870
$LiCl\cdot H_2O$	2.0	1	– 155	– 540	+ 630	–	– 855
		7	– 155	– 540	+ 640	–	– 840
		28	– 140	– 540	+ 660	–	– 840
NaCl	0.5	1	– 120	– 520	–	– 750	– 850
		7	– 150	– 515	–	– 765	– 875
		28	– 155	– 520	–	– 760	– 830
NaCl	2.0	1	– 150	– 515	+ 625	– 715	– 805
		7	– 155	– 515	–	– 735	– 825
		28	– 155	–520	–	– 715	– 825
NaCl	5.0	1	– 155	–510	–	–715; –760	– 805
		7	– 155	–510	–	–735; –760	– 810
		28	– 155	–515	–	–715; –760	– 805
KCl	2.0	1	– 145	–535	–	–700; –785	– 835
		7	– 140	–510	–	–700; –760	– 860
		28	– 150	– 545	–	–700; –760	–
$CaCl_2\cdot 6H_2O$	0.5	1	– 150	–515	–	–720; –785	–
		7	– 155	–525	–	–760; –775	– 800
		28	– 150	– 525	–	– 735	– 880

Table 1 Continued

Electrolyte/%		Hydration time/ days	Temperature interval/°C				
			115*–165	510–545	560–660	700–785	805–890
$CaCl_2 \cdot 6H_2O$	2.0	1	– 135	–510	+ 625	– 785	–
		7	– 155	–525	+ 645	–	– 830
		28	– 160	– 515	+ 650	–	– 820
		180	– 160	– 525	+ 650	–	– 830
$CaCl_2 \cdot 6H_2O$	5.0	1	– 155	– 510	+ 570	– 725	– 830
		7	– 160	–510	+ 560	–	– 820
		28	– 165	– 510	+ 565	–	– 815
		180	– 165	– 510	+ 570	–	–815
$SrCl_2$	2.0	1	– 145	–515	+ 630	–725; –795	–
		7	– 145	–520	+ 640	–715; –775	–
		28	– 150	– 545	–	– 785	– 825
$BaCl_2 \cdot 2H_2O$	2.0	1	– 135	–510	+ 630	–715; –785	–
		7	– 135	–510	+ 635	–715; –780	–
		28	– 150	– 545	–	– 775	– 810
$Ca(NO_3) \cdot 4H_2O$	2.0	1	– 140	– 510	–	– 750	– 880
		7	– 135	– 510	–	– 775	– 880
		28	–110; –150	– 535	–	– 780	–
$CaCO_3$	2.0	1	– 140	– 510	–	– 745	– 880
		7	– 145	– 510	–	– 750	– 890
		28	– 140	– 545	–	–	– 805
$CaSO_4 \cdot 2H_2O$	2.0	1	– 140	– 510	–	– 730	– 880
		7	– 140	– 510	–	– 725	– 880
		28	– 140	– 540	–	– 770	– 890

* (+) exothermic effects; (–) endothermic effects

Table 2 Thermal effects in DTA analyses of hydrated β-$2CaO\cdot SiO_2$ samples

Electrolyte/%		Hydration time/ days	Temperature interval/°C				
			120–190	400–495	505–595	620–690	805–890
	0	1	– 150[*]	– 470	–	–	– 710
		7	– 170	– 485	–	–	– 710
		28	– 170	– 485	–	–	– 710
$LiCl\cdot H_2O$	2.0	1	– 130; – 150	–	+ 595	–	– 730
		7	– 165	– 490	+ 590	–	– 735
		28	– 160	– 485	+ 595	–	– 720
NaCl	2.0	1	– 155	– 485	–	– 630	– 740
		7	– 140	– 480	–	– 650	– 750
		28	– 190	–	– 505	– 640	– 755; –780
KCl	2.0	1	– 155	– 480	–	– 635	– 745
		7	– 145	– 485	–	–	– 760
		28	– 150	– 495	–	–	– 705
$CaCl_2\cdot 6H_2O$	2.0	1	– 140	–	– 520	– 635	–
		7	– 140	– 400	– 520	– 630	–
		28	– 145	– 405	– 585	– 645	–
$SrCl_2$	2.0	1	– 160	–	– 520	+ 675	–
		7	– 155	–	– 510	– 630; + 675	–
		28	– 140	–	– 520	– 630; + 670	–
$BaCl_2\cdot 2H_2O$	2.0	1	– 120	–	– 530	– 630	–
		7	– 135	– 480	– 560	– 690	– 730
		28	– 150	– 495	– 560	– 690	– 730

Table 2 Continued

Electrolyte/%		Hydration time/ days	Temperature interval/°C				
			120–190	400–495	505–595	620–690	805–890
$Ca(NO_3)\cdot 4H_2O$	2.0	1	– 120; –150	–	– 520	– 630	– 730
		7	– 150	–	– 520	– 620	– 715
		28	– 150	–	– 520	– 620	– 715
$CaCO_3$	2.0	1	– 150	– 495	–	–630	–715
		7	– 150	– 475	–	–630	–730
		28	– 150	– 475	–	–630	–730
$CaSO_4\cdot 2H_2O$	2.0	1	– 130; – 150	– 470	–	–	– 710
		7	– 135; – 150	– 470	–	– 630	– 705
		28	– 150	– 470	–	– 630	– 730

* (+) exothermic effects; (–) endothermic effects

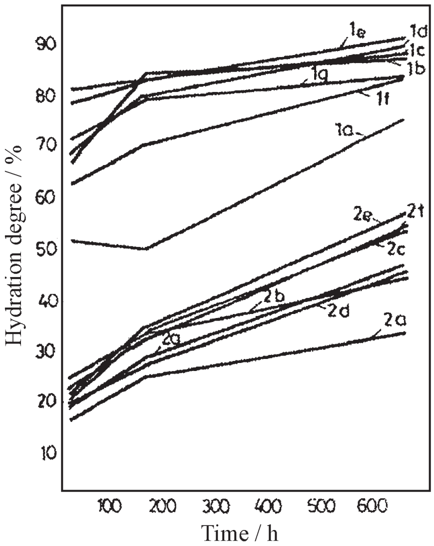

Fig. 3 Influence of alkali metal and alkaline earth metal chloride admixtures upon hydration of C_3S and β-C_2S: C_3S (1a), C_3S with 2% LiCl (1b), 2% NaCl (1c), 2% KCl (1d), 2% $CaCl_2$ (1e), 2% $SrCl_2$ (1f) or 2% $BaCl_2$ (1g) and β-C_2S (2a), β-C_2S with 2% LiCl (2b), 2% NaCl (2c), 2% KCl (2d), 2% $CaCl_2$ (2e), 2% $SrCl_2$ (2f) or 2% $BaCl_2$ (2g)

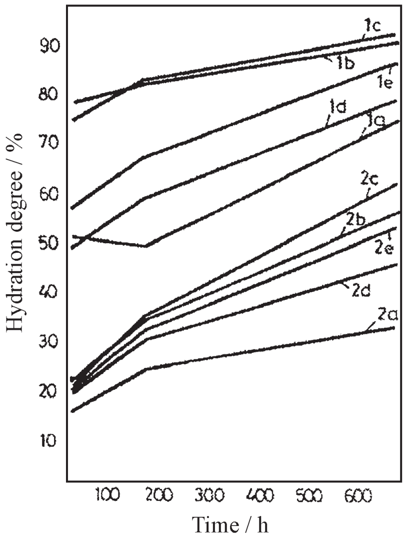

Fig. 4 Influence of calcium salt admixtures upon hydration of C_3S and β-C_2S: C_3S (1a), C_3S with 2% $CaCl_2$ (1b), 2% $Ca(NO_3)_2$ (1c), 2% $CaCO_3$ (1d), 2% $CaSO_4$ (1e) and β-C_2S (2a); β-C_2S with 2% $CaCl_2$ (2b), 2% $Ca(NO_3)_2$ (2c), 2% $CaCO_3$ (2d) or 2% $CaSO_4$ (2e)

Table 3 Molar ratios CaO/SiO_2 and H_2O/SiO_2 for the resulting calcium hydrosilicates in hydrated pastes of C_3S and β-C_2S

Electrolyte/%		$3CaO \cdot SiO_2$				β-$2CaO \cdot SiO_2$			
		CaO/SiO_2		H_2O/SiO_2		CaO/SiO_2		H_2O/SiO_2	
		1 day	28 days	1 day	28 days	1 day	28 days	1 day	28 days
–		1.01	1.63	1.25	1.68	0.50	1.70	0.60	1.76
$LiCl \cdot H_2O$	–2.0	1.47	1.83	1.80	1.86	0.63	1.77	0.65	1.79
NaCl	–0.5	1.59	1.65	1.69	1.74	–	–	–	–
NaCl	–2.0	1.46	1.79	1.55	1.87	0.56	1.83	0.70	1.81
NaCl	–5.0	1.52	1.79	1.61	1.87	–	–	–	–
KCl	–2.0	1.64	1.87	1.72	1.85	0.64	1.70	0.74	1.82
$CaCl_2 \cdot 6H_2O$	–0.5	1.60	1.68	1.65	1.75	–	–	–	–
$CaCl_2 \cdot 6H_2O$	–2.0	1.47	1.80	1.49	1.89	0.66	1.82	1.14	1.93
$CaCl_2 \cdot 6H_2O$	–5.0	1.31	1.75	1.42	1.77	–	–	–	–
$SrCl_2$	–2.0	1.48	1.85	1.56	1.93	0.71	1.80	1.05	1.83
$BaCl_2 \cdot 2H_2O$	–2.0	1.38	1.88	1.77	1.86	0.89	1.78	1.17	1.85
$Ca(NO_3) \cdot 4H_2O$	–2.0	1.51	2.01	1.67	1.80	0.80	1.89	1.04	1.86
$CaCO_3$	–2.0	1.52	1.81	1.61	1.91	0.60	1.75	0.59	1.84
$CaSO_4 \cdot 2H_2O$	–2.0	1.37	1.86	1.46	1.99	0.83	1.78	1.14	1.90

In the presence of electrolytes, in otherwise the same systems, besides the characteristic effects, which often are shifted, some new effects, including exothermic one, appear above 500°C. These modifications might be assigned to structural transformations corresponding to the hydrosilicates formed in the presence of electrolytes and the binding of the constitutive ions of the latter to the surface or inside the lattice of the calcium silicate hydro-compound. Thus, in the system C_3S–$CaCl_2$–water, the formation of an adsorptive complex is possible [4] on the surface of the binder particles, during the induction period of the hydration followed by a chemisorption process.

In the corresponding systems with 5% $CaCl_2$, X-ray analysis affords evidence of a complex salt $CaO{\cdot}CaCl_2{\cdot}12H_2O$ with a high-intensity peak at 4.18 Å in he X-ray pattern [3, 14–16]. Substitution of HO^- by Cl^- in the calcium hydrosilicate structure is possible in the hardening of calcium silicates in the presence of chloride-bearing admixtures. For complex ions, substitution can occur for the $[SiO_4]$ group, too: for instance, the $[SO_4]$ group may substitute the $[SiO_4]$ group. The substitution tendency depends on the volumes of the anions and their reactivity, the electric character of the cations etc. Ca^{2+} can also be substituted by other more electropositive cations.

DTA and X-ray data relating to the chemically bound water permit calculations of the hydration degree (Figs 3 and 4) and the chemical compositions of the calcium hydrosilicates, i.e. the molar ratios C/S and H/S [3] (Table 3).

The presence of electrolytes, especially in the early hardening days (1 to 7) has a significant influence upon the hydration degree and the ratios C/S and H/S for the resulting calcium hydrosilicates. As regards the hydration degree, an optimum proportion of electrolyte is suggested. Thus, increase of the $CaCl_2$ content from 0.5 to 2.0%, for instance, has a favourable influence, but increase of the $CaCl_2$ amount above 2.0, up to 5.0%, has only an insignificant influence upon the hydration degree, especially for longer hardening periods (time ≥28 days); even a decrease in the hydration degree is possible.

Generally, when electrolytes are present in the systems C_3S or β-C_2S–water the basicity of the calcium hydrosilicate increases, as can be seen from the molar ratio C/S in Table 3.

Conclusions

The present work provides new information regarding the possibility of using electrolyte admixtures in the hardening of the systems calcium silicates (C_3S or β-C_2S)–water.

The presence of electrolytes in the systems calcium silicate–water leads not only to significant shifts in the characteristic thermal effects, but also to the presence of new thermal effects above 500°C due to structural and compositional changes in the calcium hydrosilicates. These transformations are associated both with ionic substitution (anionic or cationic) in the calcium hydrosilicate lattice and with the formation of complex hydroxysalts, especially when the electrolyte content is above 2%.

The degree of hydration and the calcium hydrosilicate composition, i.e. the molar ratios C/S and H/S, are sensitively influenced by the presence of an electrolyte admixture.

The process of interaction of the calcium silicates with water is accelerated in the presence of electrolyte admixtures during the curing period applied; an exception is the admixture of calcium carbonate with a curing period shorter than 3 days in the case of tricalcium silicate samples. Increase of the electrolyte amounts within the limits used in our investigation generally leads to an acceleration of the hydration process; from this aspect there seems to be an optimum electrolyte amount to be used for longer periods of hydration.

In consequence of the increase in the ionic concentration of the solution, in the presence of electrolytes the resulting calcium hydrosilicates have a higher basicity and a higher proportion of chemically bound water in their structures.

References

1 W. Richartz, Zement Kalk Gips, 22 (1969) 447.
2 V. S. Ramachandran, RILEM. Mat. Constr. Materials Struct., 4 (1971) 3.
3 M. Muntean, ‘The hardening process in the binder – electrolyte – water systems’, Thesis, Polytechnic Institute Bucharest 1972, p. 27.
4 I. Teoreanu and M. Muntean, Silicat Ind., 39 (1974) 49.
5 I. Teoreanu and M. Muntean, Proceed. VIth Intern. Congr. Chem. Cem., Moscow, 1974, p. 51.
6 V. S. Ramachandran and Z. Chung-Mei, Il Cemento, 83 (1986) 129.
7 L. Montanaro, A. Negro and M. Regourd, Cem. Concr. Res., 18 (1988) 431.
8 I. Teoreanu and M. Muntean, Mat. Const. (Romania), 20 (1990) 101.
9 H. F. W.Taylor, ‘Chemistry of Cements’, Academic Press, London 1990.
10 V. S. Ramachandran, J. J. Beaudoin, S. L. Sarkar and Xu Almin, Il Cemento, 90 (1993) 73.
11 A. Tagnit and S. Bouraaoui, Proceed. Xth Intern. Congr. Chem. Cem., Goyheburg- Sweden, Vol. 2 (1997) p. 8.
12 L. Chen, L. Schzong and W. Yanrong, Proceed. IVth Beijing Intern. Symp. Cem. and Concr., Intern. Acad. Publishers Vol. 1, (1998) p. 307.
13 S. Tsivilis, G. Kakali, E. Chaniotakis and A. Souvaridou, J. Therm. Anal. Cal., 52 (1998) 863.
14 S. Monosi, I. Alvera and M. Collepardi, Il Cemento, 86 (1989) 97.
15 I. Teoreanu, M. Georgescu and G. Scaunasu, Rev. Roum. Chim., 16 (1971) 861.
16 Joint Comm. Diffr. Stand., Powder Diffraction., File Inorganic Phases Sets 1–5 Swarthmore, PA, USA 1974, p. 207.