

## CALORIMETRIC STUDIES OF $\beta$ - $\text{Ca}_2\text{SiO}_4$ HYDRATION IN SOLUTIONS OF ELECTROLYTES

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### Abstract

The hydration of  $\beta$ - $\text{Ca}_2\text{SiO}_4$  stabilized by thermal treatment and barium addition was studied in  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{BaCl}_2$  solutions. The heat evolution kinetics was followed by calorimetry. A considerable acceleration of the hydration process was found in the presence of electrolytes. The positive influence of barium ions was confirmed. The highest total heat output during the 3-day hydration was found for samples doped with 3 mole%  $\text{BaO}$ .

**Keywords:** calcium orthosilicate, electrolytes, hydration

### Introduction

Calcium orthosilicate is one of the constituents of Portland cement, in which it occurs in the form of belite, a metastable  $\beta$ - $\text{Ca}_2\text{SiO}_4$  polymorph. Cements with high  $\beta$ - $\text{Ca}_2\text{SiO}_4$  content exhibit several advantageous properties over conventional alite Portland cements. Unfortunately, they reveal a significantly slower strength development, though their final strengths exceed the values for standard Portland cement mortars.

Calcium orthosilicate can form five polymorphs; among them,  $\beta$ - $\text{Ca}_2\text{SiO}_4$  is metastable throughout the whole temperature range under atmospheric pressure. It is commonly accepted that this phase exhibits the highest hydraulic activity. Relative stability of  $\beta$ - $\text{Ca}_2\text{SiO}_4$  can be achieved by appropriate thermal treatment [1, 2] or by incorporation of certain foreign ions into the structure, substituting the calcium or silicon ions [3, 4]. The most frequently used  $\beta$ - $\text{Ca}_2\text{SiO}_4$  stabilizers are boron, phosphorus and chromium. Vanadium and arsenic are also fairly good stabilizers. As commonly reported, these ions occur as  $\text{Si}^{4+}$  replacements in the tetrahedra and their minimum contents that stabilize the  $\beta$ - $\text{Ca}_2\text{SiO}_4$  phase are close to 0.5 mole%. The foreign ions in the calcium orthosilicate structure influence the hydraulic activity.  $\beta$ - $\text{Ca}_2\text{SiO}_4$  containing  $\text{B}^{3+}$ ,  $\text{P}^{5+}$ ,  $\text{Cr}^{6+}$ ,  $\text{V}^{5+}$  and  $\text{As}^{5+}$  reacts with water at a lower rate than does  $\beta$ - $\text{Ca}_2\text{SiO}_4$  stabilized by thermal treatment [5]. Some acceleration of  $\beta$ - $\text{Ca}_2\text{SiO}_4$

hydration can be observed in the case of  $Ba^{2+}$ -doped samples [6]. However, the rate of hydration is still unsatisfactory.

Determination of the effects of calcium chloride, calcium nitrate and barium chloride on the hydration of barium-doped calcium orthosilicate was the aim of the present work.

## Experimental

$\beta$ - $Ca_2SiO_4$  samples stabilized by thermal treatment (rapid heating to 1100°C and rapid cooling, repeated many times) and samples doped with 1.0 mole% or 3.0 mole% barium were used as starting materials. The following formulae can be ascribed to the barium-doped calcium orthosilicate:  $Ca_{1.98}Ba_{0.02}SiO_4$  and  $Ca_{1.94}Ba_{0.06}SiO_4$ .

The syntheses were carried out in the following way: homogenized  $CaCO_3$  and silica-gel mixtures ( $CaO/SiO_2$  molar ratio=2), with or without  $BaCO_3$  (together with an equivalent amount of  $SiO_2$ , were preheated at 1000°C; the batches were subsequently pelletized and heated at 1350°C for several hours. Because of the presence of some  $\gamma$ - $Ca_2SiO_4$ , all of the samples were subjected to repeated heating and cooling at the temperature of the  $\alpha_H'$ - $Ca_2SiO_4$  to  $\alpha_L'$ - $Ca_2SiO_4$  transition. The  $\gamma$ - $Ca_2SiO_4$  content was shown by QXRD not to exceed 3%. In the  $Ca_{1.94}Ba_{0.06}SiO_4$  sample, the  $\alpha'$ - $Ca_2SiO_4$  phase was also detected. All the samples were ground to a Blaine specific surface of about 4000  $cm^2/g$ .

The heat evolution kinetics during calcium orthosilicate hydration was followed with an isothermal calorimeter sensitive to a thermal effect of  $10^{-6}$  W [7]. The hydration was carried out in 10%  $CaCl_2$ ,  $Ca(NO_3)_2$  and  $BaCl_2$  solutions at a liquid to solid ratio of 0.5, within an 80 h interval.

## Results and discussion

The results of calorimetric measurements are presented in Figs 1–3.

The set of figures relating to the hydration in particular solutions display a clear resemblance. Irrespectively of the electrolyte used, the  $dQ/dt=f(t)$  plots for the same calcium orthosilicate samples are of the same character. The heats evolved vary. The differences between the values for samples hydrated in  $Ca(NO_3)_2$  and  $BaCl_2$  are small, but the heats evolved for those hydrated in  $CaCl_2$  are much higher. The salts introduced into the  $Ca_2SiO_4-H_2O$  system cause almost total disappearance of the induction period (the flat part of the  $dQ/dt=f(t)$  curve before the highest peak) and a significant heat evolution rate increase in the acceleration stage of the hydration. The similar shape of the  $dQ/dt=f(t)$  curves for one type of calcium orthosilicate confirms the similarity of the accelerating effects of  $CaCl_2$ ,  $Ca(NO_3)_2$  and  $BaCl_2$  on  $Ca_2SiO_4$  hydration. A detailed explanation of the acceleration of calcium orthosilicate hydration in the solu-

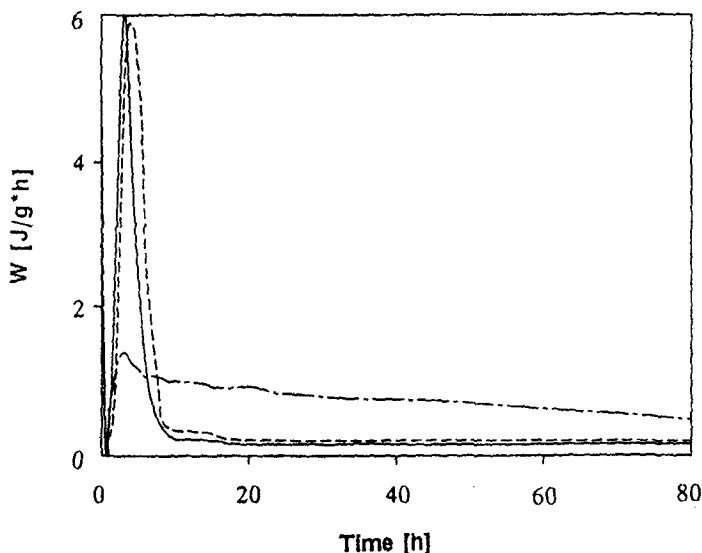


Fig. 1 Calorimetric curves of calcium orthosilicate hydration in 10%  $\text{CaCl}_2$  solution:  
 —  $\beta\text{-Ca}_2\text{SiO}_4$ , ---  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$ , - · -  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$

tions mentioned above is possible after the additional studies. It should be mentioned that, among the inorganic additions accelerating cement paste setting and hardening,  $\text{Cl}^-$  is placed before  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$ – $\text{Ba}^{2+}$  [8, 9]. However, in the

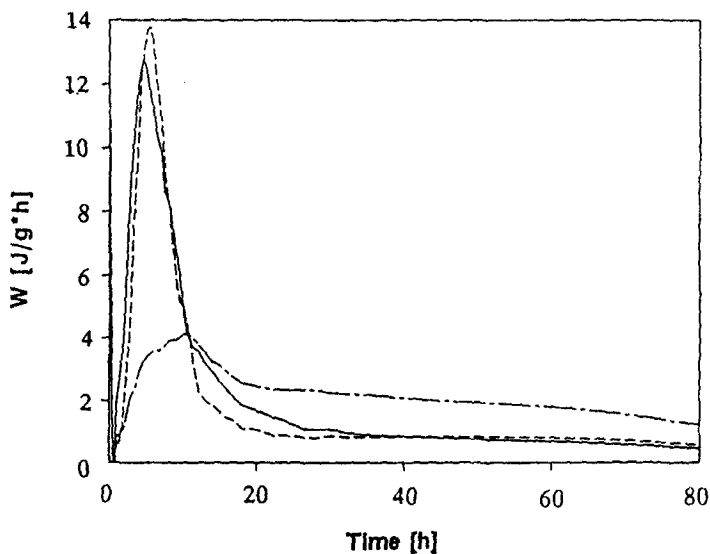


Fig. 2 Calorimetric curves of calcium orthosilicate hydration in 10%  $\text{Ca}(\text{NO}_3)_2$  solution:  
 —  $\beta\text{-Ca}_2\text{SiO}_4$ , ---  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$ , - · -  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$

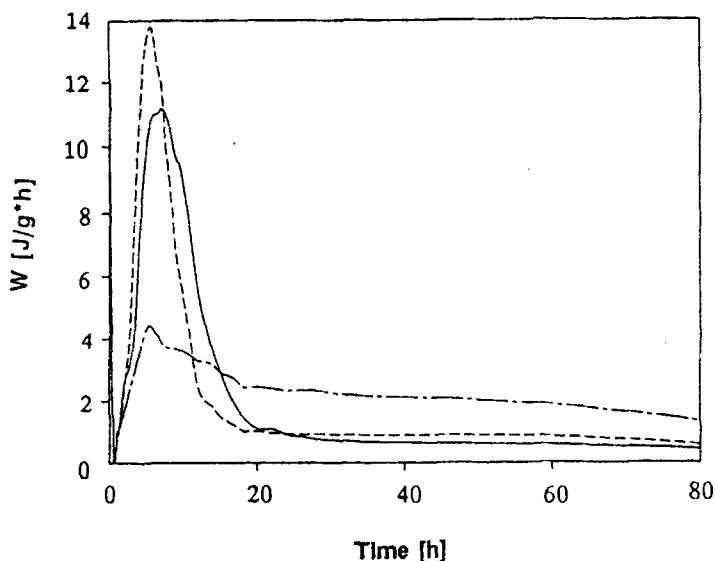


Fig. 3 Calorimetric curves of calcium orthosilicate hydration in 10%  $\text{BaCl}_2$  solution:  
 —  $\beta\text{-Ca}_2\text{SiO}_4$ , - - -  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$ , - · - ·  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$

system thus considered, the heat evolution rates were shown earlier to be lowest for the samples hydrated in  $\text{CaCl}_2$  solutions. It seems, therefore, that in the systems thus presented, a significant role in the acceleration of heat evolution should be attributed to factors other than those occurring in the system cement-water-activator.

Analysis of the calorimetric curves demonstrates the differences between the behavior of  $\beta\text{-Ca}_2\text{SiO}_4$ ,  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$  and  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$ . The heat evolution curves for  $\beta\text{-Ca}_2\text{SiO}_4$  and  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$  are of the same character; after a short induction period, the rate of heat evolution increases sharply, and then immediately decreases. The hydration of  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$  occurs in a different way. In this case too, the presence of  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{BaCl}_2$  brings about the disappearance of the induction period. However, the main peak is rather small and the amount of heat evolved decreases with time. This phenomenon is observed for all the solutions used. The relatively small differences in barium concentration in  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$  and  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$ , together with the fact that barium quickly enters the liquid phase as a hydroxide and forms  $\text{BaO} \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$  with a molar ratio  $\text{BaO}/\text{SiO}_2$  of about 1 [10], cannot change the calorimetric curves significantly. The changes are clearly visible, probably because of the presence of  $\alpha'\text{-Ca}_2\text{SiO}_4$ . It should be stressed that quantitative evaluation of  $\alpha'\text{-Ca}_2\text{SiO}_4$  is difficult, because of the coincidence of the XRD peaks. It should also be mentioned that the total heat evolved during the

Table 1 Heat evolved during the calcium orthosilicate hydration in solutions of electrolytes

Time/h	Heat evolved / J·g <sup>-1</sup>											
	β-Ca <sub>2</sub> SiO <sub>4</sub>				β-Ca <sub>1.98</sub> Ba <sub>0.02</sub> SiO <sub>4</sub>				Ca <sub>1.94</sub> Ba <sub>0.06</sub> SiO <sub>4</sub>			
	CaCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	BaCl <sub>2</sub>		CaCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	BaCl <sub>2</sub>		CaCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	BaCl <sub>2</sub>	
1	0.53	19.98	18.33		0.55	20.94	21.34		0.59	22.02	23.65	
3	3.72	29.44	22.92		6.72	25.15	26.22		2.76	24.38	26.99	
6	18.27	63.91	46.38		17.41	58.91	59.77		6.45	33.23	38.06	
12	23.48	106.66	104.59		20.01	100.41	101.15		12.46	55.34	60.13	
24	25.93	132.38	127.68		22.43	116.84	120.27		22.93	87.06	91.57	
48	31.34	153.92	143.42		28.14	136.28	132.85		41.78	138.22	142.08	
60	34.53	160.35	149.89		32.46	145.14	149.67		49.51	161.46	164.41	
72	36.89	168.31	156.01		36.32	153.79	155.56		55.27	179.52	184.61	

long-lasting hydration is significantly higher for  $\text{Ca}_{1.94}\text{Ba}_{0.06}\text{SiO}_4$  than for  $\beta\text{-Ca}_2\text{SiO}_4$  and  $\beta\text{-Ca}_{1.98}\text{Ba}_{0.02}\text{SiO}_4$  (see Table 1).

It also emerges from the data in Table 1 that, during the first hour of hydration, the highest heat output should be attributed to the sample with the highest barium content. This can be caused by the leaching of barium ions from the calcium orthosilicate structure, as found earlier in studies of the liquid phase separating from hydrating suspensions [6]. During the period 6–24 h from the beginning of the hydration process, the highest heat output was found for  $\beta\text{-Ca}_2\text{SiO}_4$  stabilized by thermal treatment.

## Conclusions

1. In the presence of  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{BaCl}_2$ , the hydration of calcium orthosilicate is accelerated and the induction period is limited. The heats evolved from the samples hydrated in  $\text{BaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  solutions are similar and significantly higher than that in the presence of  $\text{CaCl}_2$  solution.

2. Incorporation of barium into the  $\beta\text{-Ca}_2\text{SiO}_4$  structure brings about a heat evolution increase during the first hour of hydration.

3. The highest total heat evolved during the 3-day hydration is attributed to the samples doped with 3 mole% of barium.

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**Zusammenfassung** — In  $\text{CaCl}_2$ -,  $\text{Ca}(\text{NO}_3)_2$ - und  $\text{BaCl}_2$ -Lösungen wurde nach Zusatz von Barium und Hitzestabilisierung die Hydratation von  $\beta\text{-Ca}_2\text{SiO}_4$  untersucht. Die Kinetik der freigesetzten Wärme wurde mittels Kalorimetrie verfolgt. Im Beisein von Elektrolyten wurde eine beträchtliche Beschleunigung des Hydratationsprozesses beobachtet. Der positive Effekt der Bariumionen wurde festgestellt. Die größte Gesamtwärmefreisetzung wurde während der 3-tägigen Hydratation für Proben gefunden, die mit 3 Mol% BaO versetzt waren.