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THERMOGRAVIMETRIC STUDIES OF THE TRICALCIUM SILICATE HYDRATION IN THE PRESENCE OF SOLID ADDITIVES

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The calcium hydroxide content in the tricalcium silicate pastes hydrating with the amorphous silica and solid calcium hydroxide addition were determined using the TG method. The effect of the accelerated $Ca(OH)_2$ growth at the lower silica contents was proved. The significant hydration rate increase at higher silica contents was also confirmed.

The tricalcium silicate Ca_3SiO_5 hydration at early stages results in the formation of the calcium silicate hydrates (amorphous, of variable CaO/SiO_2 ratio and water content) and calcium hydroxide [1]. Such factors, as water content, temperature and presence of admixtures influence the kinetics of reactions and subsequently the amount and properties of particular hydration products.

In the presented work the studies of the tricalcium silicate hydration with the amorphous silica were continued. The amorphous silica addition brings about the formation of the hydrated calcium silicates, thus accelerating the tricalcium silicate decomposition in water [2, 3]. According to some earlier works [4], the silica addition inhibits the calcium hydroxide crystallization. However, in the light of our more detailed studies, the "poisoning" effect of silica on the calcium hydroxide nuclei has not been confirmed [5, 6]. The results prove that the calcium hydroxide content in the pastes with some silica is higher as compared with those without silica. On the other side, at the silica addition of ca. 5% and more the calcium hydroxide content decrease is observed.

In order to resolve the problem of $Ca(OH)_2$ crystallization in the pastes containing tricalcium silicate and silica, the samples of Ca_3SiO_5 and (0.1-10%) SiO_2 were mixed together with the constant 2% $Ca(OH)_2$ addition.

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The tricalcium silicate sample was synthesized at 1550° from the homogenized and pelletized $CaCO_3$ + SiO_2 mixture, calcined preliminary.

The tricalcium silicate and the additives of calcium hydroxide and silica were mixed with water to form the suspensions at the water to solid ratio 10 and shaked. After the 5 minutes to 24 hours hydration the samples were filtered and the solid residues were treated with acetone and ether to remove the unreacted water. The solid samples were dried additionally at 60° and then analysed by means of Mettler thermoanalyser to determine the water bound in the hydration products – the calcium silicate hydrate and calcium hydroxide. The unhydrated tricalcium silicate was also determined by QXRD. The results are shown in Tables 1, 2.

Table 1 The calcium hydroxide contents in the $Ca_3SiO_5+Ca(OH)_2+SiO_2$ pastes as the function of time and SiO_2 addition (C = CaO, S = SiO_2, H = H_2O)

Samples	% $Ca(OH)_2$ after the time of hydration				
	5'	1h	3h	7h	24h
C_3S	0.12	0.48	1.23	2.38	10.02
C_3S + 2%CH	2.30	2.62	3.12	6.07	12.96
C_3S + 2%CH + 0.1%S	2.26	3.28	3.20	6.33	14.10
C_3S + 2%CH + 0.5%S	2.13	2.79	3.17	5.25	12.46
C_3S + 2%CH + 1%S	2.21	2.95	3.77	5.58	15.91
C_3S + 2%CH + 5%S	1.97	2.46	3.03	6.40	16.73
C_3S + 2%CH + 10%S	0.49	0.82	1.48	5.90	17.06

Table 2 The hydration degree of the tricalcium silicate in the mixtures with calcium hydroxide and silica

Samples	Hydration degree, %	
	7h	24h
C_3S	14	36
C_3S + 2%CH	30	48
C_3S + 2%CH + 0.1%S	35	50
C_3S + 2%CH + 0.5%S	37	46
C_3S + 2%CH + 1%S	37	58
C_3S + 2%CH + 5%S	46	65
C_3S + 2%CH + 10%S	52	80

As it can be easily seen, the crystalline calcium hydroxide brings about the acceleration of calcium hydroxide formation at the first hours of hydration if the SiO_2 addition does not exceed 5%. The small silica addition even promotes the $Ca(OH)_2$ growth. At higher SiO_2 content the calcium hydroxide dissolves as soon as the solid sample is mixed with water. This effect is the consequence of the high reactivity of the amorphous silica toward the alkaline $Ca(OH)_2$ solution. At lower SiO_2 content the concentration of the calcium hydroxide resulting from the tricalcium silicate hydrolysis is sufficient to saturate the silica added and form the calcium silicate hydrated phase.

After the 7 hours hydration the calcium hydroxide contents in the samples with 5% and 10% SiO_2 are similar to those in other samples. After 24 hours hydration the $Ca(OH)_2$ contents increase with increasing SiO_2 addition can be observed. The hydration degree is clearly higher in the samples with 5% and 10% SiO_2. This effect indicates that the formation of the significant amount of calcium silicate hydrated phase takes place. Unfortunately, this phase content, because of its variable chemical composition, cannot be calculated from the TG measurements.

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Zusammenfassung — Unter Anwendung von TG wurde der Calciumhydroxidgehalt bei der Hydratation von Tricalciumsilikat mit Zusätzen von amorphem Siliziumdioxid und festem Calciumhydroxid ermittelt. Der Einfluß des beschleunigten $Ca(OH)_2$ Wachstumes bei niedrigeren Siliziumdioxidgehalten wurde erwiesen. Eine eindeutige Erhöhung der Hydratationsgeschwindigkeit bei höheren Siliziumdioxidgehalten wurde ebenfalls bestätigt.