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THERMAL METHODS AND MICROCALORIMETRY APPLICATION IN THE STUDIES OF LOW ENERGY CEMENTS

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In the DTA studies of the clinkerization process the values of enthalpy attributed to the particular stages of clinker synthesis were determined and the energy consumption decrease due to the modification of the phase composition was calculated for 400 J/g.

The activation of the low energy cement by Ba addition was shown using microcalorimetry and thermal methods.

Keywords: cement clinkerization, DTA, microcalorimetry

Introduction

One way of the energy consumption lowering in the portland cement clinker production is the change of the traditional clinker composition by the replacement of the main component i.e. alite Ca_3SiO_5 by belite Ca_2SiO_4 of lower enthalpy of formation [1]. Unfortunately, the reactivity of belite to water is much more lower than that of alite. Therefore, the studies on the activation process of belite phase are carried out [2].

The barium containing by-product was introduced to the raw mixture for clinkerization with aim to reduce the clinker formation temperature, to modify the phase composition of clinker and to improve the belite phase hydraulic properties.

DTA and TG methods were used in the studies of clinker formation. The enthalpies of particular reactions occurring on heating, as well as the total enthalpy of clinkerization were calculated. The heat evaluation during the hydration of cements produced from the clinkers with and without Ba containing additions was followed using differential calorimetry. The hydration products were studied by DTA and TG methods.

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Experimental

The dynamic studies of the raw mixtures were carried out using the Setaram Microanalyzer (DTA sensitivity — 100 mV, heating rate — 5 deg/min, nitrogen atmosphere, in the range 20°–1450°C). The DTA curves are shown in Fig. 1. The heat evolution during the hydration process was studied in the nonisothermal-nonadiabatic differential microcalorimeter type BMR (constructed in the Institute of Physical Chemistry in Warsaw), on the pastes at water to solid ratio 0.5, at 25°C. The dehydration of hydrated samples with aim to evaluate the amount of the hydration product (hydrated silicates, aluminates, calcium hydroxide) was investigated using the Mettler thermoanalyser.

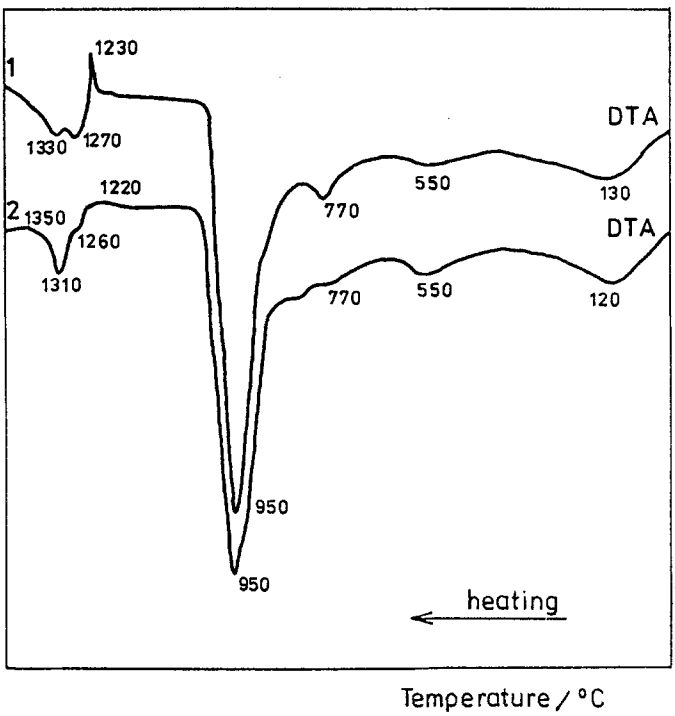

Fig. 1 DTA curves of samples subjected to the clinkerization
1 – reference raw mixture containing calcium carbonate and clay, 2 – raw mixture with reduced calcium carbonate content and barite by-product

The endothermic peaks attributed to the clayed minerals decomposition at 120°, 550° and 770°C are seen in Fig. 1. The calcium carbonate decomposition begins at 860°C with the peak maximum at 950°C and its intensity is higher for the Ba containing mixture. At 1230°C the exothermic peak corresponding to the reaction between CaO and acid oxides and effect of the melt formation appears.

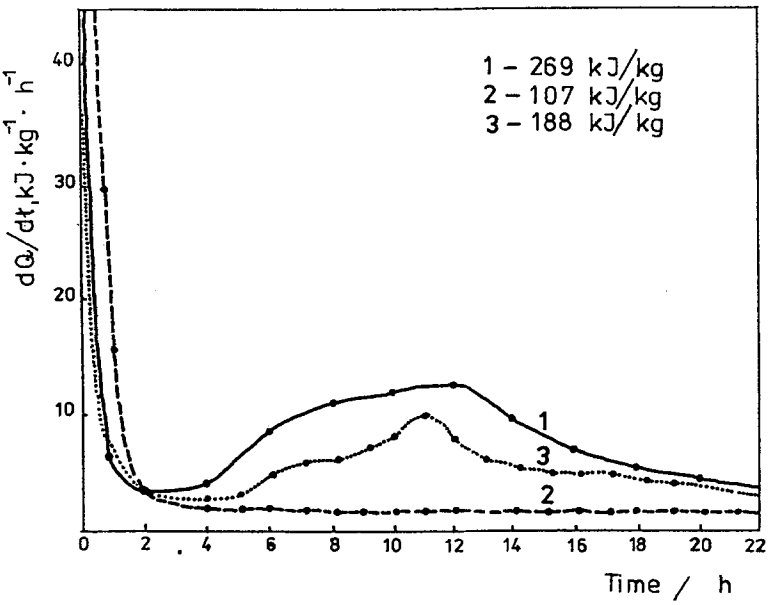

Fig. 2 Microcalorimetric curves of cements with different clinkers
1 – classic clinkers, 2 – clinker with high belite content, 3 – clinker with high belite content modified by barium

As it results from the DTA curve, the clinkerization process in the Ba containing mixture is completed at 1350°C, i.e. at lower temperature that in the case of the traditional portland cement clinker formation. In Table 1 the enthalpies of processes occurring in the particular temperature ranges, leading to the clinker formation are listed.

Table 1 Heat consumption during the clinkerization process

Temperature range / °C	Heat consumption in J/g	
	Mixture I (reference)	Mixture II (with Ba)
20– 400	394	393
400– 600	243	233
600– 800	471	489
800–1100	1649	1658
1100–1350	628	586
1350–1450	253	285
Total enthalpy 20°–1450°C	3637	3530
Enthalpy of clinkerization	3673 (to 1450°C)	3246 (to 1350°C)

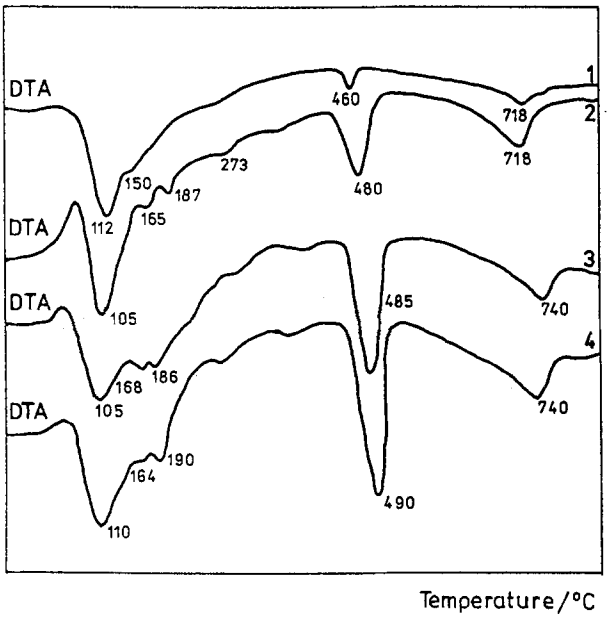

Fig. 3 DTA curves of hydrated cement pastes with increased belite content after 1, 3, 7 and 28 days hydration

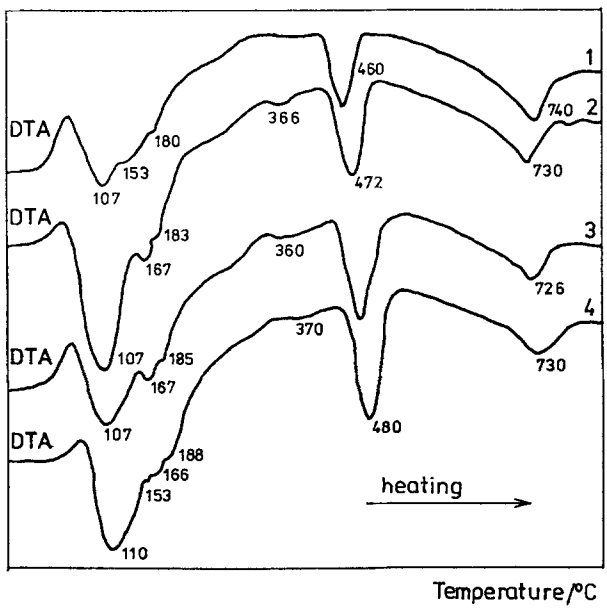

Fig. 4 DTA curves of hydrated cement pastes with increased belite content after 1, 3, 7 and 28 days hydration

Conclusion

Heat evolution accompanying the reaction with water in the presence of increased belite content is highly reduced as compared with the results for the classic cement and shows the deceleration of hydration process. As the Ba containing addition is introduced to the cement clinker, the hydraulic activity of material increases. It is proved not only by use of microcalorimetry but also in the DTA-TG studies of the hydration products (Figs 3, 4). The hydration products decomposition peaks areas for the both series of samples show that at the presence of Ba the hydration process is accelerated as compared to the belite cement sample.

References

1 J. P. Meric, Ciment, Beton, Platre et Chaux, 1 (1987) 764.
2 J. Stark and A. Mueller, X IBAUSIL, Weimar 1988.

Zusammenfassung — In einer DTA-Studie des Klinkerbildungsprozesses wurden die Enthalpiewerte der einzelnen Stufen der Klinkersynthese bestimmt. Die ermittelte Abnahme der Energieaufnahme für die Änderung der Phasenzusammensetzung beträgt 400 J/g. Mittels Mikrokalorimetrie und thermischen Methoden konnte die Aktivierung des energetisch niedrig liegenden Zementes durch Zusatz von Ba nachgewiesen werden.