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SECONDARY RAW MATERIALS IN CEMENT INDUSTRY

Evaluation of their effect on the sintering and hydration processes by thermal analysis

M. Perraki[1]*, T. Perraki*[1]*, K. Kolovos*[2]*, S. Tsivilis*[2]*, G. Kakali*[2]*

[1]National Technical University of Athens, Mining Engineering Department, 9 Heroon Polytechniou St., 15773 Athens, Greece
[2]National Technical University of Athens, Chemical Engineering Department, 9 Heroon Polytechniou St., 15773 Athens, Greece

Abstract

The sintering and hydration processes of a modified cement raw mix were examined using thermal analysis techniques. One reference and four modified mixtures, prepared by mixing the reference sample with 0.5, 1.0, 1.5 and 2.0 % *w*/*w* of a wolframite-stibnite mineral were studied. The clinkering reactions were recorded and the total enthalpy change during the sintering was determined by means of a differential scanning calorimetry. The combined water and the $Ca(OH)_2$ content in samples hydrated for 1 to 28 days were determined, using thermogravimetry. As it is concluded, the effect of the added mineral on the sintering and hydration reactions can be fully recorded and evaluated using thermal analysis.

Keywords: cement raw mix, DSC, hydration, sintering, TG

Introduction

Cement production requires a high input of energy for the sintering of the raw meal. An attractive approach to energy conservation is the addition of selected materials in the raw mix aiming either to the decrease of the final burning temperature or the acceleration of the sintering reactions. Ash slag waste, granulated blast furnace slag, converted slags, ore dust, coal preparation wastes and worked out moulding sands are being used in some of the rotary kiln plants, either alone or in binary/ternary combinations during clinkerization. A lot of non-conventional reactive industrial wastes can also be used in order to improve the performance of the shaft kiln [1–3]. These materials have a variety of chemical and mineralogical composition and their exact effect on the sintering of the raw meal and the hydration of the cement is difficult to be evaluated in advance. The prediction of the burnability of a cement raw meal and

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* Author for correspondence: E-mail: kakali@central.ntua.gr

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the reactivity of the cement is therefore of great technical and economic importance for the management of cement plants, but many difficulties arise from the complexibility of chemical reactions during the formation and hydration of clinker.

In practice, the reactivity of the raw mix is evaluated based on the determination of free lime content (lime not incorporated in clinker phases) after burning at a specific temperature for a constant time. The free lime content is indicative of the end-point but not of the whole sintering process. Since large enthalpy changes are associated with the burning reactions, instrumental thermal analysis could provide a useful tool for the study of the sintering process and the characterization of cement raw mixtures [4–6].

Cement is a system composed of numerous minerals which react with water at different rates, give hydration products of different composition and crystallinity and influence the engineering properties of the final product in different ways. The two most important clinker components primarily responsible for the cement setting and strength development respectively, are tricalcium aluminate (C_3A)[**] and tricalcium silicate (C_3S). C_3S and C_3A react with water, in the presence of gypsum, according to the following equations (1)–(3). It must be noticed that the reactions are much more complex than shown below [7].

$$C_3S \xrightarrow{H_2O} C{-}S{-}H + n\mathrm{CH} \text{ (calcium hydroxide)} \tag{1}$$

$$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_3A \cdot 3C\underline{S}H_{32} \text{ (ettringite)} \tag{2}$$

$$C_3A \cdot 3C\underline{S}H_{32} + 2C_3A + 4H \rightarrow 3C_3A \cdot C\underline{S}H_{12} \text{ (monosulphate)} \tag{3}$$

The hydration rate of cement can be evaluated by measuring the mass loss of hydrated samples up to 800°C by means of a thermobalance [8]. The amount of calcium hydroxide (dehydroxylation peak ~500°C) is directly related to the amount of calcium silicate that has reacted with water. Calcium hydroxide is easily carbonated and transformed to calcium carbonate, therefore the amount of calcium hydroxide which is equivalent to calcium carbonate (decomposition peak ~700°C) must be counted in. The water bound in the hydrated products is removed in the temperature range 100–300°C. The dehydration of pore water takes place at ~100 °C, while water chemically bound in the hydration products is removed at higher temperatures according to the bond energy. There is a strong overlapping of DSC and DTG peaks in this area, however the total mass loss is a measure of the rate of hydration, while any changes of the number and shape of peaks indicate changes of the stoichiometry in the hydrated products.

In this paper the application of thermal analysis (DSC, TG and DTG) in order to record the effect of mineral additions on clinker formation and cement hydration is discussed.

[**] Cement chemistry notation: $C=CaO$, $A=Al_2O_3$, $S=SiO_2$, $F=Fe_2O_3$, $\underline{S}=SO_3$, $H=H_2O$

Experimental

An industrial cement raw meal was used as reference sample. The chemical composition of the raw mix as well as the mineral composition (according to Bogue) and the moduli of the obtained clinker is presented in Table 1.

Table 1 Characteristics of the raw mix and the produced clinker

Raw mix		Clinker			
Chemical composition / %*w*/*w*		Mineral composition (Bogue)/ %*w*/*w*		Moduli	
SiO_2	13.76	C_3S	71.1	LSF	0.981
Al_2O_3	3.23	C_2S	7.7	SM	2.42
Fe_2O_3	2.45	C_3A	6.9	AR	1.32
CaO	43.11	C_4AF	11.6	HM	2.22
MgO	0.55				
K_2O	0.28				
LOI	35.62				

A wolframite–stibnite assemblage was selected in order to introduce the elements W, Sb and S in the cement raw mix. Appropriate samples were collected after a complete mineralogical and chemical characterization of the ores, coming from Kilkis region, Greece. Table 2 presents the principal constituent and the chemical composition of the mineral.

Table 2 Principal constituent and chemical composition of the selected mineral

Name	Principal constituent	Chemical composition
Wolframite-stibnite assemblage	$(FeMn)WO_4–Sb_2S_3$	WO_3: 47%, Sb_2O_3: 20% Fe_2O_3: 13%

One reference and four modified mixtures, prepared by mixing the reference sample with 0.5, 1.0, 1.5 and 2.0 % *w*/*w* of the above mineral, were examined. The sintering reactions in all samples were recorded by means of differential thermal analysis using a Mettler Toledo TGA/SDTA 851 instrument. The temperature was raised at a constant rate (10°C min^{-1}) from ambient to 1450°C. The experiments were conducted in static atmosphere.

The produced clinkers were coground with 5% *w*/*w* gypsum in a pro-pilot plant ball mill of 5 kg capacity. The gypsum was of industrial origin (98% *w*/*w* $Ca_2SO_4 \cdot 2H_2O$, 46.7% *w*/*w* SO_3). The fineness of all the produced cements was found to be in the range between 3500 and 3700 $cm^2\ g^{-1}$ (Blaine). Pastes were prepared by mixing cement and deionized water. A water-to-cement ratio (*w*/*c*) of 0.4 was retained for all pastes. After 6 h, the cement cores were put in polythene containers (vials), sealed hermetically and wet-cured at 20°C. Samples, hydrated for periods of 1, 2, 7, and 28 days, were subjected to acetone and isopropyl ether treatment, in order to remove the excess water, and then dried for 24 h in vacuum. Thermogravimetric analysis (TG) was applied for the determination of non-evaporable water, calcium hydroxide and calcium carbonate in dried cement paste samples using the Mettler Toledo TGA/SDTA 851 instrument. The samples (~50 mg) were heated over the range 20°C to 900°C at a constant rate of 15°C min^{-1} in an atmosphere of carbon dioxide free nitrogen, flowing in 90 $\text{cm}^3\ \text{min}^{-1}$.

Results and discussion

Sintering process

Figure 1 presents the DSC curves of the reference sample and the sample containing 0.5% of the wolframite–stibnite assemblage. In the DSC curve of a cement raw mix the following stages are distinguished:

- a broad endothermic effect attributed to the dehydroxylation of clays (200–600°C),
- the big endothermic reaction of the limestone dissociation (800–1000°C),
- one or more exothermic reactions (1200–1350°C) connected with the belite (C_2S) formation,
- an endothermic reaction just after the last exothermic reaction (1300–1400°C) associated with the partial melting of the sample.

The first two stages depend on the chemical and mineralogical characteristics of the clays and the limestone respectively, and as it was expected, they were identical in all samples. The most important stages are the third and the fourth which are directly associated with the clinkerization process. The evaluation of the DSC curve of a cement raw mix comprises the following stages:

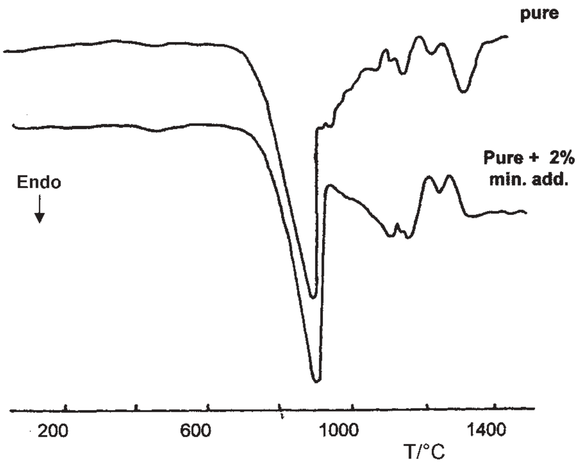

Fig. 1 DSC curves of pure and modified (mineral addition: 0.5%) cement raw mixes

1. Recording of the sintering reactions
2. Determination of reaction temperature and enthalpy
3. Estimation of enthalpy change during sintering
4. Tracing of changes caused by the modification of the raw mix

Stages 1 and 2 are very simple to perform in any DSC instrument. Stage 3 is a software option in the specific instrument. Table 3 presents the enthalpy changes during the thermal treatment of the samples. Stage 4 involves the comparison of the pure sample's curve with the modified samples' curves and the evaluation of any recorded differences.

Table 3 Enthalpy change during the thermal treatment of the samples (J g^{-1})

Mineral addition in the raw mix/ %*w/w*				
0	0.5	1.0	1.5	2.0
–2326.5	–1515.8	–1612.8	–1798.2	–1998.6

After the evaluation and comparison of all DSC curves, the following results are drawn:

- In all modified samples the reactions associated with the decomposition of $CaCO_3$ (in the temperature range of 800–900°C) and clinkerization (1200–1450°C) are recorded, suggesting satisfactory burning and clinkerization of all samples.
- The added mineral do not affect the limestone decomposition and the belite formation.
- In modified mixtures the formation of the melt is shifted to lower temperature and overlapped with the belite formation. This fact indicates that the constituents of the added mineral are dissolved in the liquid phase, affecting mainly its formation.
- The added mineral decreases the enthalpy change during sintering. This positive effect is more intense in the case of low addition percentage.

Hydration process

The evaluation of the TG-DTG curves consists of the following steps:

1. Determination of the total combined water: this is the total water incorporated in the cement paste. It corresponds directly to the mass loss up to 550°C. The mass loss in the range 600–700°C, if any, corresponds to the CO_2 of $CaCO_3$ and must be converted to CO_2 the equivalent $Ca(OH)_2$ and then to equivalent H_2O.
2. Determination of the $Ca(OH)_2$: it is found by the mass loss in the range 400–550°C, converted to calcium hydroxide and then added to the calcium hydroxide that has been carbonated.
3. Determination of water combined in the hydration products (other then calcium hydroxide): it corresponds directly to the mass loss up to 300°C. Any changes of the water content in the hydration products indicate that the kind and/or the stoichiometry of these compounds have changed.

4. Tracing of modifications in hydrated products: Hydrated ordinary Portland cement is a complex mineral comprised mainly of calcium silicate hydrates (C–S–H). C–S–H is nearly an amorphous material, containing water of various energy levels which is removed in various stages. These stages cannot be traced on the thermogravimetric curve, due to extensive overlapping, but they are shown on the differential thermogravimetric curve.

Table 4 Total compound water, calcium hydroxide and water in the hydration products in relation to the content of the added mineral in the raw sample and the age of hydration

Mineral content/ %*w*/*w*	Hydration age/days			
	1	2	3	4
	Compound water/%*w*/*w*			
–	15.24	16.08	17.71	24.29
0.5	15.10	16.69	18.75	24.88
1.0	15.72	16.00	17.89	23.36
1.5	14.78	15.26	17.48	23.94
	$Ca(OH)_2$/%*w*/*w*			
–	21.35	23.43	26.09	26.80
0.5	20.56	21.93	23.93	24.98
1.0	18.99	19.30	24.17	23.68
1.5	18.34	21.54	23.18	23.68
2.0	18.91	20.10	22.69	22.12
	Water in hyadrated products/%*w*/*w*			
–	10.05	12.38	13.56	17.77
0.5	10.00	12.55	12.93	18.80
1.0	11.10	11.55	12.01	17.60
1.5	10.32	10.02	11.85	18.18
2.0	9.89	10.86	11.26	17.12

Figure 2 presents the TG and DTG curves of the modified cement (2% *w*/*w* of the mineral in the raw mixture) after 1 and 28 days of hydration. As it is shown, only one of these samples was carbonated. The carbonation of the paste is an accidental event that may take place during the preparation of the paste or during the grinding of the paste previous to the TG measurement. The DTG curves (up to 200°C) indicate the difference of the hydration products which is due to the different age of hydration.

Table 4 presents the percentage of total compound water, calcium hydroxide and water in the hydration products in relation to the content of the added mineral in the raw sample and the age of hydration. As it is shown, small additions of the added mineral (up to 1%) do not significantly affect the total rate of hydration. As the min-

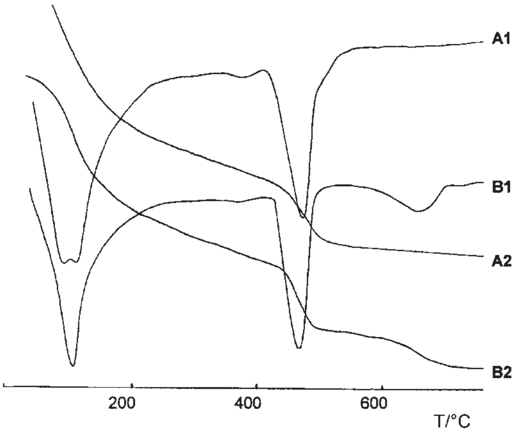

Fig. 2 TG (1) and DTG (2) curves of cement pastes (mineral addition: 2%). A: after 28 days, B: after 1 day

eral content in the raw mix increases, the hydration tends to slow down, as it is indicated by the progressive decrease of water and calcium hydroxide content in the pastes. The stronger effect of the added mineral on the calcium hydroxide content indicates that it affects especially the hydration of silicate compounds.

Conclusions

As it is generally concluded from the present study, DSC, TG and DTG are very useful techniques for the evaluation of the sintering and hydration of modified cement raw mixture. Their application in the case of a cement raw mixture containing a wolframite-stibnite assemblage leads to the following conclusions:

- The added mineral do not affect the solid state reactions during the sintering but it has a positive effect on the formation of the melt. The modified raw mixtures require less energy during sintering.
- The added mineral exerts a slight retarding effect on the hydration of cement and especially of the silicate compounds.

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