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DIFFERENTIAL SCANNING CALORIMETRY
A useful tool for prediction of the reactivity of cement raw meal

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Abstract

DSC was used in order to evaluate the reactivity of cement raw meal. Two groups of samples were studied: five industrial raw meals for ordinary Portland cement production, with similar compositions, but differences in granulometry; and five industrial raw meals for white Portland cement production, with similar granulometric features, but different compositions. The burnability indices of the samples were correlated with certain data obtained from the DSC curves. It is concluded that the DSC curve data, and especially the temperature and enthalpy effect of belite formation, are strongly correlated with the burnability of the cement raw meal. The temperature of belite formation is affected by chemical and mineralogical factors, while the enthalpy effect is additionally affected by the fineness of the raw meal.

Keywords: burnability, cement raw meal, DSC

Introduction

In the manufacture of Portland cement, the burning process accounts for up to 60% of the total energy involved. Prediction of the reactivity of a cement raw meal is therefore of great technical and economic importance for the management of cement plants.

Portland cement clinker is formed by firing a calcareous material mixed with a siliceous one to a temperature of 1300–1500°C. In principle, the clinker comprises four phases: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and a ferrite phase approximating to the composition C_4AF*.

As Bucchi [1] has clearly shown, the process of burning of cement raw meal consists of a series of partial processes:

* Cement chemistry notation: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3

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- drying of argillaceous materials,
- decomposition of carbonates,
- solid-state reactions,
- reactions in the presence of liquid phase,
- crystallization.

The rates of the above reactions and the tendency of the material to undergo conversion are strongly affected by the fineness, and by the chemical and mineralogical compositions of the raw meal. The laws governing the processes of solid-solid diffusion and also those between solids and liquids explain the influence of such factors on the reactivity of a raw meal [2]. The raw meal chemical composition is mainly characterized by three factors: the lime saturation factor (LSF), the silica ratio (SR) and the alumina ratio (AR). LSF is intimately related with the proportion of free lime, C_2S and C_3S. An increase in LSF causes an increase in the burning temperature and consequently an increase in the energy consumed. SR determines the relation between the calcium silicate and the sum of the clinker interstitial body and is also related to the development of the liquid phase. A high SR decreases the burnability of a raw meal. AR controls the composition and nature of the liquid phase. The higher AR, the greater the proportion of aluminates, the more viscous the liquid phase and the higher the burning temperature [3]. As concerns the effect of the fineness of a raw meal, it has been shown that the rate limestone decomposition and diffusive phenomena are inversely proportional to the fourth power of the particle diameter, while the rates of dissolution of solids in the liquid are directly proportional to the fourth power of the particle diameter [1, 4].

In practice, determination of the clinkering behaviour of industrial mixtures is based on the residue of free lime after burning at a specific temperature for a constant time. Various mathematical equations have been proposed for the prediction of burnability [3, 5–7].

Since large enthalpy changes are associated with the burning reactions, instrumental thermal analysis could provide a useful tool for study of a clinkering process and the characterization of cement raw mixtures [8, 9].

In the present paper, DSC has been used in order to record the clinkering reactions of cement raw meals with different granulometric features and chemical compositions. The aim of the study was to investigate the correlation of the reactivity and the relative characteristics of the raw meal with certain data obtained from the DSC curves.

Experimental

Two groups of samples were studied. The first group consisted of five industrial mixtures for OPC production, named RM1–RM5, which have the same mineralogical and chemical compositions, but different granulometric features. The second group included five industrial raw mixtures, for white cement produc-

tion, referred to as RMI–RMV, having different chemical compositions, but similar granulometric characteristics. The chemical compositions of the raw samples, their finenesses, expressed as the residue at 90 μm, and the mineralogical compositions of the sintered samples, determined according to Bogue, are presented in Tables 1, 2 and 3, respectively.

Table 1 Chemical compositions of raw samples

Sample code	CaO/	SiO_2/	Al_2O_3/	Fe_2O_3/	Loss on ignition/
			%		
RM1–RM5	43.11	14.90	3.22	2.12	35.12
RMI	43.21	15.77	1.92	0.08	34.20
RMII	43.32	15.97	2.02	0.10	34.83
RMIII	43.21	16.16	2.28	0.12	34.81
RMIV	43.41	15.34	3.01	0.14	34.10
RMV	42.48	14.90	4.02	0.12	34.20

Table 2 Finenesses of raw samples (% residue at 90 μm)

Sample	RM1	RM2	RM3	RM4	RM5	RMI–RMV
R_{90}/%	18.5	13.5	11.0	8.0	5.5	7.5

Table 3 Mineralogical compositions and moduli of sintered samples

Sample code	C_3S/	C_2S/	C_3A/	C_4AF/	Liquid/	LSF	SR	AR
			%					
RM1–RM5	52.87	26.52	9.23	10.20	12.56	90.58	2.51	1.23
RMI	66.42	19.63	7.62	0.54	7.70	92.28	7.9	22.6
RMII	63.29	22.53	7.96	0.64	7.66	91.83	7.5	20.6
RMIII	57.67	27.57	8.96	0.56	8.04	89.99	6.7	19.0
RMIV	54.10	25.92	11.74	0.46	10.60	91.02	4.9	21.6
RMV	49.41	27.66	15.89	0.40	13.23	91.27	3.6	34.6

The % residue free lime (fCaO) of the above samples was determined, after thermal treatment to 1350, 1400, 1450 and 1500°C, and the burnability index (BI) was estimated according to Eq. (1). Table 4 presents the fCaO contents, at different temperatures and the relative BI for all samples.

$$BI = 3.75 \frac{C1 + C2 + 2C3 + 3C4}{(C1 - C4)^{1/4}} \quad (1)$$

where C1, C2, C3, C4: %fCaO at 1350, 1400, 1450 and 1500°C, respectively.

The clinkering reactions were recorded by means of a Netzsch STA409C differential scanning calorimeter. The temperature was raised at a constant rate (10°C min^{-1}) from ambient to 1400°C. The experiments were conducted in a static atmosphere. α-Al_2O_3 was used as reference material.

Table 4 Residual contents of free lime (%fCaO) and burnability indices (BI) of samples

Sample code	%fCaO				BI
	1350°C	1400°C	1450°C	1500°C	
RM1	8.7	6.7	4.7	3.0	81
RM2	7.8	5.2	3.3	2.1	64
RM3	7.0	4.9	2.9	1.8	56
RM4	6.8	4.0	2.5	1.3	48
RM5	6.3	3.8	2.2	1.1	44
RMV	9.9	7.1	5.2	3.9	93
RMIV	13.6	10.4	8.6	7.8	156
RMIII	12.2	11.3	10.1	8.3	184
RMII	16.1	14.4	13.7	12.7	264
RMI	16.4	15.5	14.3	13.4	286

The compounds formed at specific temperatures, related to the recorded reactions, were identified in cooled samples by means of X-ray diffraction.

Results and discussion

The DSC curves of cement raw meals exhibit three clearly-defined stages. The endothermic effect between 600°C and 800°C is attributed to the decomposition of $CaCO_3$. The following exothermic reactions are associated with the formation of belite, while the endothermic effect at higher temperatures is attributed to the formation of liquid and to the formation and development of alite crystals. The exothermic effects in the cooling curve are connected with crystallization of the liquid phase. The differences between the studied samples are located in the temperature range 1000–1400°C. This range of the heating curves is presented in Fig. 1.

Figure 2 depicts, inductively, the X-ray diffraction patterns of sample RM4 sintered at different temperatures. As indicated by the identification of the compounds produced, C_2S is mostly formed in the region 1200–1300°C, and C_3S in the region 1300–1400°C. The formation of C_2S shifts towards higher temperatures in white PC samples, while C_3S is not detected in appreciable amounts up to 1400°C.

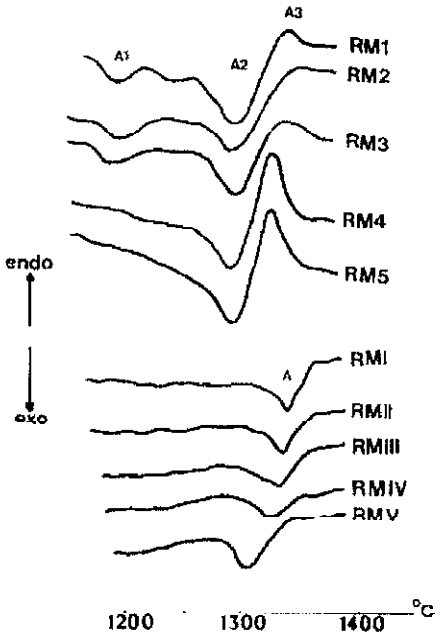

Fig. 1 DSC curves of raw samples

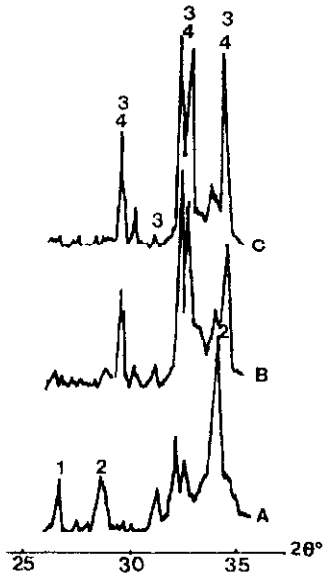

Fig. 2 X-RD patterns of sample RM4 sintered at 1200°C (A), 1300°C (B) and 1400°C (C); 1 – SiO_2, 2 – CaO as $Ca(OH)_2$, 3 – C_3S, 4 – C_2S

Ordinary PC samples

Figure 1 reveals that a decrease in the fineness of a sample causes an increase in the number of recorded exo reactions. This is caused by the different reactivities of the raw meals. It is known that in materials which sinter easily the preliminary formation of belite takes place gradually, over a wide temperature range and there is therefore a lack of well-defined peaks. In less reactive materials, the preliminary formation of belite is assumed to take place in one or more well-defined steps. Two stages of preliminary formation of belite are recorded for sample RM1, each for samples RM2 and RM3, and non for samples RM4 and RM5. The higher reactivity of the finer samples was confirmed by the determination of fCaO. The endo peak connected with the formation of the liquid phase is better recorded for the finer and therefore more reactive samples RM5 and RM4.

Table 5 gives the DSC curve data to be correlated to BI. These are the temperatures (T) and the relative areas of the peaks recorded by DSC (A_1, A_2 formation of belite; A_3 formation of liquid phase) and the total area (A_1+A_2) associated with the formation of belite. The limits of integration are determined by means of the first derivative of the DSC curve as concerns a linear baseline. The investigation of the correlation of BI with the variables given in Table 5 and the fineness of the samples is based on Pearson correlation analysis (α=0.05).

Table 5 Temperatures (T) and areas (A*) of DSC peaks of OPC samples

Sample code	T_1/ °C	A_1/ mVs mg^{-1}	T_2/ °C	A_2/ mVs mg^{-1}	A_1+A_2/ mVs mg^{-1}	T_3/ °C	A_3/ mVs mg^{-1}
RM1	1186–1231	4.7593	1289	7.1124	11.8717	1336	5.3188
RM2	1185	3.0363	1287	4.8322	7.8685	1349	4.6923
RM3	1186	2.6266	1294	5.8788	8.5024	1334	4.3210
RM4			1290	7.3607	7.3607	1317	6.6948
RM5			1293	6.6287	6.6287	1322	5.9142

*A_1: Preliminary formation of belite. Exo reaction
A_2: Main formation of belite. Exo reaction
A_3: Formation of liquid phase. Endo reaction

Table 6 Pearson product-moment correlation matrix for OPC samples

	A_1	T_2	A_2	A_1+A_2	T_3	A_3	R_{90}
BI	0.9578	–0.5482	0.0744	0.9329	0.6509	–0.4310	0.9929

Table 6 presents the results derived from the Pearson correlation test between BI, R_{90}, the peak temperatures and the areas corresponding to preliminary belite formation, total belite formation and melt formation, respectively. As indicated

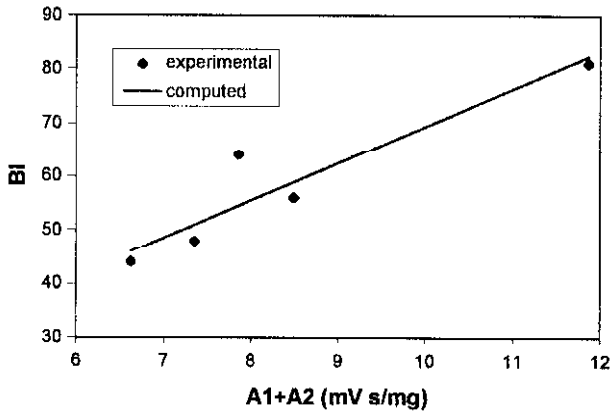

Fig. 3 BI of OPC samples in relation to the total peak area of belite formation

by the values of the Pearson coefficients, BI is strongly related to the fineness and the peak areas connected with belite formation, especially the total one. The peak temperatures and the melt formation area do not seem to be affected by the fineness and BI of the samples. Regression analysis was used in order to model the raw meal BI as a function of (A_1+A_2). The equation BI=6.92824 (A_1+A_2) determines BI through (A_1+A_2) with satisfactory accuracy (R^2=0.9938). Finally, Fig. 3 presents BI in relation to A_1+A_2.

White PC clinker

The main difference between the clinkering processes of ordinary and white cement raw mixtures is the difficulty of melt formation in the latter. The low content of Fe_2O_3 in combination with the high AR causes an increase in the melting temperature and an increase in the melt viscosity [10]. As a result, the formation of the liquid phase is not clearly recorded up to 1400°C.

Table 7 Temperature (T) and area (A*) of DSC peak for white PC samples

Sample code	RMI	RMII	RMIII	RMIV	RMV
T/°C	1343	1337	1333	1316	1305
A/mV s mg^{-1}	10.311	9.7415	8.3286	5.6598	4.7079

*A: Main formation of belite. Exo reaction

Table 8 Pearson product-moment correlation matrix for white PC samples

	T	A	C_3S	C_2S	C_4AF	SR	AR
BI	0.9509	0.9648	0.9961	−0.8958	−0.7566	0.9615	−0.6514
T			0.9660	−0.7463	−0.7017	0.9967	−0.7306
A			0.9761	−0.7862	−0.7795	0.9918	−0.6531

An investigation of the correlation of BI with the chemical-mineralogical variables and with the DSC curve data (T and A) of the samples (presented in Table 7) is given in Table 8. It is concluded that BI is strongly correlated with C_3S and SR and weakly negatively correlated with AR. Table 8 shows that the DSC curve can be used to evaluate the raw meal burnability since the T and A values are strongly correlated with the BI of the samples. Regression analysis demonstrates that the equation BI=25.78324 A furnishes the best performance (R^2=0.9889). Figure 4 presents BI in relation to A.

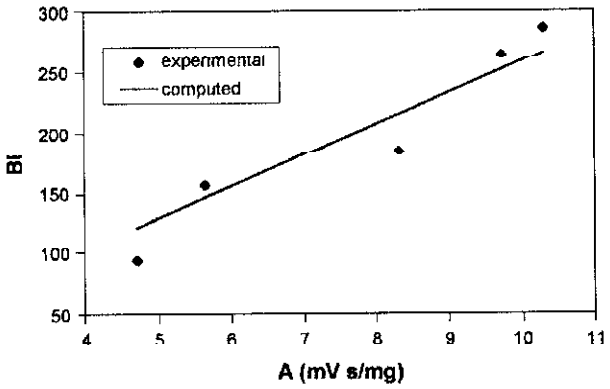

Fig. 4 BI of white PC samples in relation to the peak area of belite formation

It has been established that the DSC curve is related both qualitatively and quantitatively with the cement raw meal reactivity. In both cases, the evaluation is based mainly on the formation of belite. The number of recorded exoreactions connected with belite formation is inversely proportional to the reactivity of the raw mixtures. Additionally, the characteristics of these peaks (temperature and area) can be used to estimate the burnability index. The temperature is affected by chemico-mineralogical factors, while the area is affected by both the chemico-mineralogical composition and fineness. Further investigations are needed in order to establish the correlation for samples that vary in composition and fineness simultaneously.

Conclusions

The following conclusions can be drawn from the present study:

The DSC curve data can be used to evaluate the burnability of a cement raw meal. The evaluation is based on the reactions connected with belite formation.

The fineness of the raw meal affects only the enthalpy effect of belite formation and not the temperature of this reaction.

The burnability index of cement raw meal can be estimated from the enthalpy effect associated with belite formation.

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