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APPLICATION OF THERMAL ANALYSIS TO THE CEMENT INDUSTRY

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Methods involving heat measurements have been applied in the cement industry for a long time. Differential thermal analysis (DTA) is used to explain the clinkering reactions, but it is a dynamic method which thus does not allow measurements and calculations of the thermal balance of the reactions to be made. In contrast, high temperature microcalorimetry may be used to measure the enthalpy of the clinkering reactions of industrial raw materials. Results obtained by using this technique allow us to determine the thermal profile of clinkering reactions in the kiln and to quantify the heat exchange in the solid material during its burning.

Low temperature conduction microcalorimetry gives information on the hydration mechanism of the cement pastes. In this paper, we review the applications of thermal analysis in the cement industry paying special attention to new methods such as high temperature microcalorimetry.

Keywords: cement industry, high temperature microcalorimetry

Introduction

Thermal analysis techniques are widely used in cement industry. They include differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermodilatometry (TD), thermogravimetric (TG) and calorimetry (adiabatic and isothermal).

Some of these techniques are applied to the raw materials and to the fuel and lead to a better understanding of the manufacture of the clinker. DTA is used to study the burnability of the raw materials, TG to study the rate of decarbonation; thermodilatometry to understand sintering phenomena, high temperature microcalorimetry to establish the thermal balance of the kiln and bomb calorimetry to measure the energy content of the fuel.

Other methods are applied to the cement itself after mixing with water. The 'Langavant' calorimeter is used to measure the increase of the temperature in the mortar

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or the concrete; DSC is used to identify the hydration products; TG to study the rate of hydration and low temperature (< 100°C) conduction calorimetry helps to understand the mechanism of hydration and interaction with admixtures.

Some of these techniques are used routinely in cement industry, some are less well known. This paper describes the applications of these thermal analysis techniques to the cement industry with special reference being made to conduction microcalorimetry.

Cement and its production

DTA is used to help to understand the mechanism of the clinkering reaction [1] and to estimate the burnability of the raw mix. The burnability of a cement raw mix quantifies the ease or the difficulty of the mass transfer of its constituents to the clinker phases. The burnability of raw mixes is of great importance in cement technology because the burning temperature and the residence time in the burning zone of the kiln depend on the burnability of the raw materials. The behaviour of a raw mix during the sintering process is influenced by its chemical, mineralogical and granulometric composition. Variation in the burnability affects kiln operation, the refractory lining, fuel consumption and clinker quality. Each cement raw mix burns in its own way resulting in variation of clinker quality. By convention burnability is measured by determining the amount of lime which has not combined after a certain time at a certain temperature: the free lime. High temperature differential thermal analysis is an useful tool to compare the burnability of different raw meal. Figure 1 shows a typical DTA curve for an industrial raw meal.

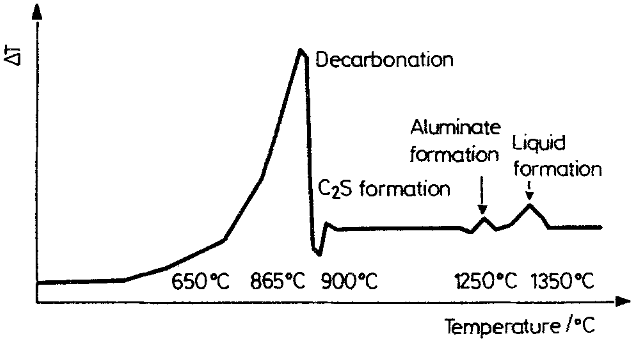

Fig. 1 Typical DTA curve of an industrial Portland cement raw mix

We see the endothermic peak of carbonate decomposition, followed by the exothermic peak of dicalcium silicate formation. At higher temperatures we detect the formation of aluminate or calcium alumino-ferrite (very small heat exchange), and the formation of a small quantity of a liquid phase. The position and intensity of the peaks give good information about the burnability of the raw meal. DTA has also been used to determine the enthalpy of clinkering reactions [2], but it is not the best method to measure this parameter because it is a dynamic method (not isothermal).

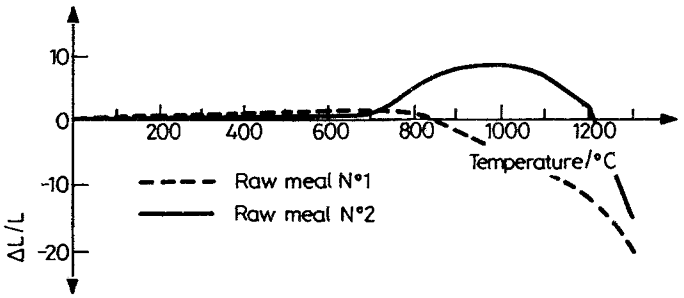

Fig. 2 Examples of thermodilatometry curves for two Portland cement raw mixes

During the clinkering reactions, a quantity of liquid phase forms: this leads to shrinkage which can be measured by thermodilatometry. Figure 2 shows the thermodilatometry curve of two industrial raw mixes. By means of this technique, it is possible to know the temperature at which the liquid phase forms as well as its quantity. Consequently we have information on the kinetics of the clinkering reactions. The results obtained correlate very well with those obtained in plants by the measurement of apparent density (litre weight, i.e. the weight of the product contained in a volume of one 1000 cm^3).

The most important condition to obtain a good burning is to reach the right temperature during the right time.

Excessively high temperature leads to prohibitively high energy costs. Excessively low sintering temperature have a detrimental effect on cement reactivity due to a high free lime content. To achieve good burning conditions, it is necessary to know:

i) the energy of combustion of the fuel

ii) the enthalpy of formation of the clinker compounds (thermal balance of the kiln)

To measure the energy content of the combustible, a classical adiabatic calorimeter (also called a bomb calorimeter) is used. The substance to be studied is placed in a pressure vessel and brought into contact with an igniter wire which is attached to two electrodes. An excess of oxygen is supplied to the substance in order to ensure total combustion. The bomb is placed in a water filled container equipped with a thermometer and stirrer. The substance is then ignited and completely burnt. The rise in temperature of the water bath is measured and represents a direct measure of the heat content of the substance.

The use of a calorimeter to determine the energy content of the substance used for burning makes it possible to utilize the calorific value of the fuel as a controlled variable

[3]. It allows the heat consumption to be optimized and therefore contributes to reducing the cost of the process.

In order to calculate the thermal balance of the kiln, we need the enthalpy of formation of the main compounds of the clinker: tricalcium silicate, dicalcium silicate, tricalcium aluminate and calcium alumino-ferrite. To find this information, we have used the technique of dissolution in molten lead borate. The defined compound and its constituents are dissolved in molten lead borate at 800°C and the heat of dissolution is measured by conduction calorimetry. The difference between the two figures gives the enthalpy of formation of the compound, provided the reaction goes to completion [4]. This may be checked by scanning electron microscopy. If this precaution is not taken, discrepancies between the results could occur. Table 1 shows the enthalpy of formation for the main cement compounds. We can see that the enthalpy of formation of tricalcium aluminate and calcium alumino-ferrite are rather small and compensate for each other. As opposite the reaction forming C2S and C3S are strongly exothermic.

Table 1 Enthalpy of formation of the main Portland cement compounds

		Enthalpy of formation j/g
Dicalcium silicate	C2S	–692
Tricalcium silicate	C3S	–546
Tricalcium aluminate	C3A	72
Calcium alumino ferrite	C4AE	–97

The heat exchange during the clinkering reaction is measured by the drop technique in a multidetector high temperature calorimeter. This equipment includes a furnace with carbon resistor. The temperature of the kiln is fixed and the sample (a few mg), which is initially at room temperature, is dropped into the kiln. A cell with 56 thermocouples records the heat exchanged by the sample to reach the defined temperature. In Fig. 3, the upper curve, shows the results obtained for an industrial raw meal. The bottom curve shows the curve for the clinker: it corresponds to the heat which could be recovered from the cooler [5, 6]. In the curve corresponding to the burning of the raw meal, we can see the endothermic part which corresponds to the decarbonation of the limestone and the exothermic part which corresponds to the formation of dicalcium silicate. These two reactions occur simultaneously but with a different rate thus, although the peaks overlap with each other, nevertheless the exothermic peak due to the formation of dicalcium silicate can be seen very distinctly.

It is interesting to relate these experiments to the real industrial process. Several processes exist and we have chosen three of the more recent systems: long dry kiln, kiln with heat exchanger, and kiln with a precalciner. In Fig. 4 we have tried to represent the reactions occurring in different zones of the kiln and the cooler: preheating, calcination, transition zone, burning zone and cooling zone. We have plotted the temperature in the different zones, the % of dicalcium silicate (belite) and the total enthalpy measured by isothermal calorimetry. During calcination, the raw meal requires energy to decarbonate, but simultaneously, the formation of dicalcium silicate releases energy. The maximum rate of belite formation corresponds to the decrease in the slope of the curve representing the total enthalpy of the reactions.

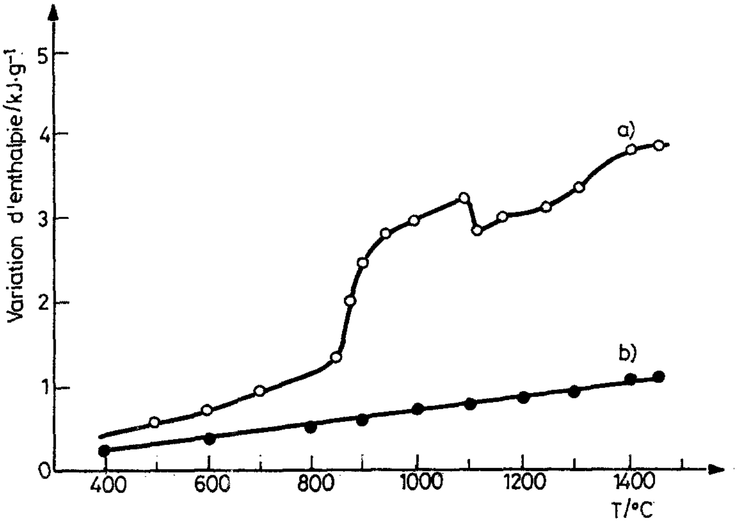

Fig. 3 Variation of enthalpy *vs.* temperature for: a) Portland cement raw mix, b) Portland cement clinker

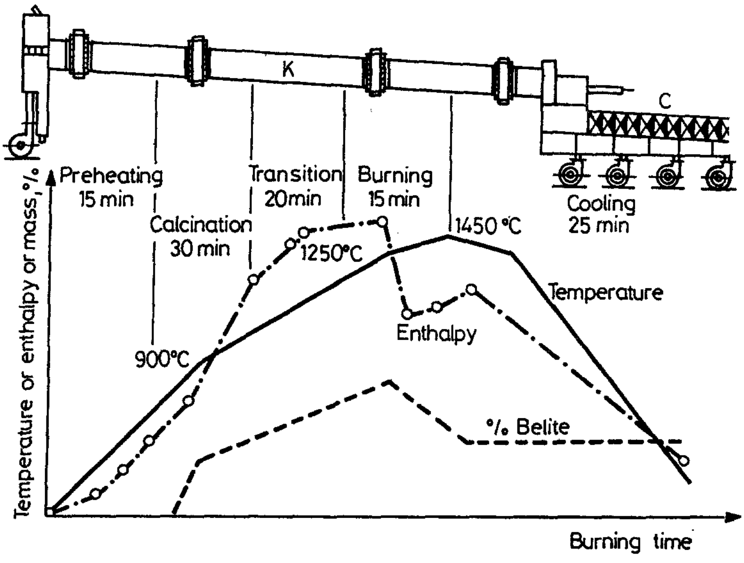

Fig. 4 Enthalpy of clinker formation in a long dry kiln. K = rotary kiln, C = cooler

Figure 5 represents the clinkering reaction in kiln with a preheater. There are notable differences. The preheating lasts less than one minute, the calcination time is about the same, the transition zone is shorter than the total residence time. Therefore in this case, we see that the zone where the heat exchange is high is shorter.

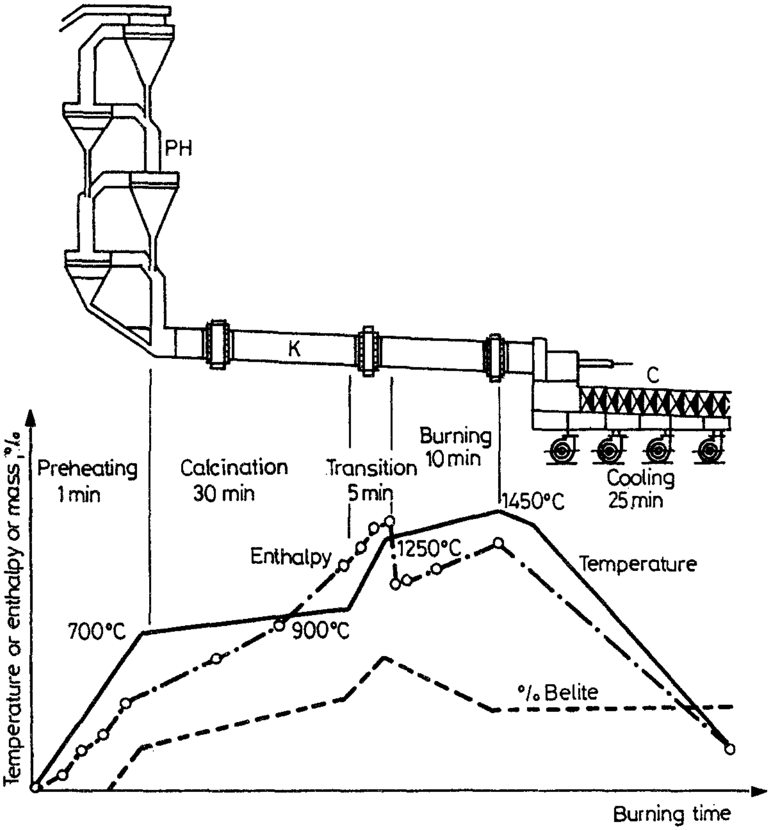

Fig. 5 Enthalpy of clinker formation in a, kiln with preheater. K = Kiln; C = Cooler; PH = Preheater

Figure 6 shows a kiln equipped with a precalciner. There are large differences between this and the previous two processes especially the shortening of the calcination zone and most importantly heat exchange occurs at the beginning of the kiln.

These examples have been, of course, oversimplified but illustrate how the information from the isothermal calorimeter can be used.

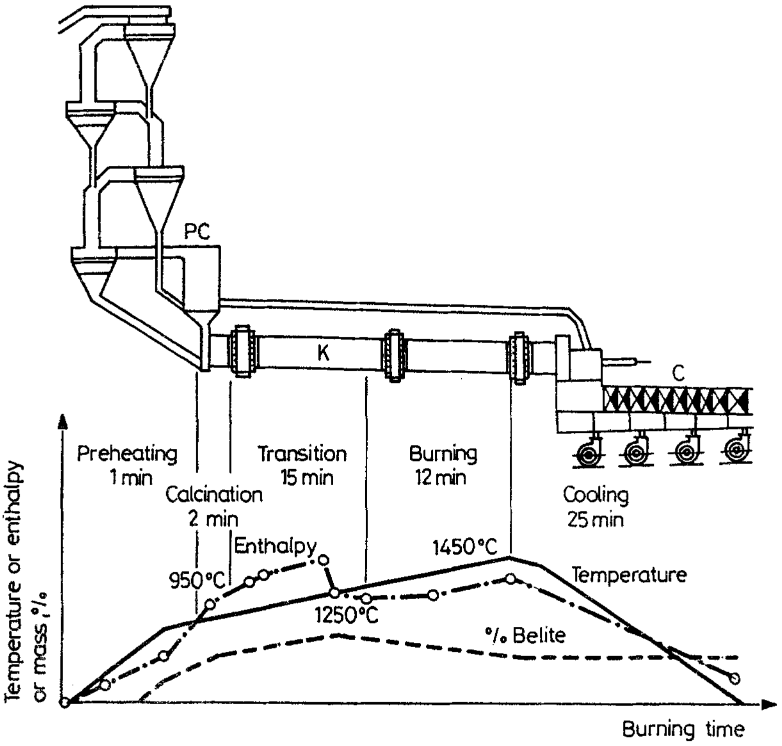

Fig. 6 Enthalpy of clinker formation in a kiln with precalciner. K = Kiln; C = Cooler; PC = Precalciner

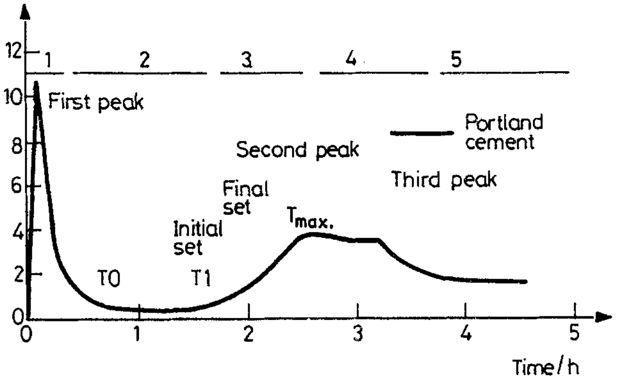

Fig. 7 Isothermal conduction calorimetry of Portland cement hydration

Cement and its use

When Portland cement is mixed with water, its constituent compounds undergo a series of chemical reactions which are responsible for the hardening of concrete [7]. The hydration reactions of Portland cement are all exothermic. Thus during the hardening process the concrete is continually warmed by the internal heat generated. The rate of heat evolution is the important parameter.

With increasing temperature, the early strength of the cement increases due to the fact the cement hydrates more rapidly, but if the temperature increases too much, detrimental effects occur due to a non uniform distribution of hydration products, leading to weak zones in the cement and low strengths. It is thus important to control the heat released during the hydration of the cement. This is done by using the Langavant calorimeter, an adiabatic calorimeter in which the temperature increase of a defined quantity of cement mortar or paste is measured. This technique is used as a routine quality control test.

In order to understand the mechanism of the reaction of hydration, it is necessary to:

i) identify the hydration products
ii) follow the rate of the hydration

DTA or DSC are the techniques most commonly used to identify the hydrated products and these applications have been widely described for both Portland and high alumina cements [8, 9].

The measurement of the heat of hydration by conduction calorimetry can reveal information about the chemical reactions occurring during hydration. Conduction calorimetry has the advantage of giving estimates of both the heat evolved and the instantaneous rate of heat liberation at any time. Most Portland cements produce over 50% of their heat of hydration in the first three days of hydration, so a continuous record during this time gives interesting information on the rate of the hydration.

Figure 7 shows a typical heat evolution curve for the hydration of Portland cement.

The different stages of the hydration can be shown in the conduction calorimetry curve.

Stage 1: Within the first minutes [1, 2], there is a rapid evolution of heat culminating in a peak. This rapid release of heat corresponds to the heats of wetting, the hydration of hemihydrate to calcium sulphate dihydrate, the formation of ettringite, the initial hydrolysis of C3S and the release of calcium ions into solution.

Stage 2: This stage is often called dormant period because, according to conduction calorimetry, there is no or very little heat exchange. Some authors have wrongly interpreted these results as an absence of activity. In reality, the releases of calcium ions continues but at a slower rate, limited by the ability of the anhydrous product to interact with available water through the outer layer. The thin layer of 'C–S–H' (hydrated calcium silicate) that makes up the outer layer is probably a polymerization of the hydrolysed silicate groups.

Stage 3 is characterized by an accelerated hydration of C3S and the initiation of calcium hydroxide crystallization. Simultaneously a transformation of the 'C–S–H' gel occurs exposing additional surface area of the anhydrous particles.

Stages 4 and 5 represent a deceleration of these diffusion controlled reactions.

A third peak can sometimes be observed. It has often been associated with the conversion of calcium trisulfoaluminate (ettringite) into monocalcium aluminate: this explanation seems to be incorrect and this peak is more likely associated with a new formation of ettringite. Another shoulder which is not visible in this curve may occur and is associated with the hydration of calcium alumino-ferrite [10].

Low temperature conduction calorimetry has been widely used [11–13] and can find application in the study of general cement hydration, setting behaviour, stiffening [14], the influence of gypsum [15, 16], the influence of fineness [17], the effect of alkalis [18, 19], the effect of admixtures [20–22], special cements: high alumina cements [23], oil well cements [24] and blended cements [25, 26]. Most of these applications have been described in the referenced paper and summarized by J. Bensted [14].

Conclusions

1) Thermal analysis and especially conduction calorimetry has a wide range of application in cement chemistry.

2) DTA or DSC can be used to determine the burnability of the raw meal, multidetector high temperature calorimetry allows the precise calculation of the thermal balance of industrial kilns.

3) Low temperature isothermal calorimetry can be used to study the hydration of the cement, its reactivity, the effects of cement surface area as well as phenomena such as stiffening. This technique is also useful for studying the effects of admixtures upon cement hydration.

4) When quantitative interpretation is attempted, attention must be paid to chemical reactions occurring. Thus calorimetry should be used in conjunction with other methods such as electron microscopy, X-ray diffraction, IR spectroscopy, or mass spectrometry.

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Zusammenfassung — Seit langer Zeit werden in der Zementindustrie Verfahren mit Wärmemessung angewendet. Zur Erforschung der Verschlackungsreaktionen wird DTA verwendet, was jedoch ein dynamisches Verfahren ist und keine Messungen und Berechnungen bezüglich des thermischen Gleichgewichtes erlaubt. Im Gegensatz dazu kann Hochtemperatur-Mikrokalorimetrie zur Messung der Enthalpie von Verschlackungsreaktionen industrieller Rohstoffe dienen. Mit Hilfe der durch diese Methode erlangten Resultate kann das thermische Profil von Verschlackungsreaktionen im Kiln und der Wärmeaustausch im Festmaterial beim Brennen bestimmt werden.

Niedertemperatur-Konduktions-Mikrokalorimetrie liefert Informationen über den Hydratationsmechanismus von Zementleim. Unter spezieller Beachtung neuer Methoden, wie z.B. der Hochtemperatur-Mikrokalorimetrie, wird in diesem Artikel ein Überblick über die Anwendungen der Thermoanalyse in der Zementindustrie gegeben.