

Sonderdruck  
aus

Zement-Kalk-Gips  
Juni/August 1990

# **Kalorimetrie im Zementlabor**

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Calorimétrie dans le laboratoire de cimenterie

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# Calorimetry in the cement laboratory

## 1. Cement Production

Cement production, and cement clinker burning in particular, involves continuous processes; special importance is placed on controlling the flows material with respect to quantity and composition on the basis of continuously-monitored quality characteristics.

The processes which are important for clinker formation only proceed at temperatures between 1400 and 1450°C. From this it is easy to see the importance of exact knowledge of the heat requirement of the process.

## 2. Thermal economy of the cement kiln – gross calorific value as a controlled variable

Depending on the type of kiln and the process used the heat requirement per tonne of clinker lies between 3.0 and 6.2 GJ per tonne of clinker. The most important condition for “correct” burning is, however, attainment of the sintering temperature of 1400-1450°C. Excessively high temperatures not only have a negative effect on the process to the detriment of the energy costs, but can also produce “dead-burnt” cement. Excessively low sintering temperatures have a similar negative effect on cement reactivity. In previous processes the combustion air has normally been used as the controlled variable for the temperature. In this case the most important controlled variable would be the excess air ratio  $\lambda$ . The use of a calorimeter to determine the energy content of the substances used for burning makes it possible to utilize the gross calorific value of the fuel as an additional controlled variable. This is an advantage from two points of view. Firstly, it allows the heat consumption to be optimized and therefore contributes to reducing the cost of the process and, secondly – given the great inertia of the kiln system – accurate and continuous balancing of the heat during the process is a more suitable means of attaining the sintering temperature reliably.

## 3. History of calorimetry

A device for determining the energy content of materials was first developed over 100 years ago. The unit then used for energy was the calorie, so this device was named a calorimeter. Nowadays the energy unit is the Joule, but the designation for the equipment for measuring energy remains as before, a calorimeter. Although the measuring principle has stayed unchanged until today, the equipment has changed very greatly over the course of years.

## 4. Theory of calorimetry

It is well known that energy, or quantity of heat, cannot be measured directly. However, it is possible to measure energy by using other physical effects which change in size as a function of the quantity of energy supplied. The method of measurement used in all current calorimeters is based on this concept. Temperature is used as the measured secondary variable.

## 5. Principle of the measurement

A precisely weighed quantity of the substance to be determined is placed in a pressure vessel, the so-called calorimeter bomb. The substance is brought into contact with an igniter wire which is attached to two electrodes. As the intention is to measure the combustion energy it is necessary to ensure that the substance is completely burnt. An excess of oxygen is therefore supplied to the substance.

After the lid has been closed the bomb is therefore filled with oxygen at approximately 30 bar. This quantity of oxygen ensures that even quite large quantities are completely burnt. The filled bomb is placed in a water-filled container which is equipped with a thermometer and stirrer (Fig. 1). The rise in temperature of the water bath is measured after the substance has been ignited and completely burnt. The difference in temperature is a direct measure of the heat content of the substance.

## 6. Simultaneous analyses

The chemically combined energy is analyzed by combustion in pure oxygen. At the same time there is an oxidative decomposition of the organically combined elements in the substance. This decomposition makes it possible to carry out several simultaneous, or subsequent, analyses on one and the same sample. The organically combined halogens can be absorbed in a suitable absorption solution in the bomb and determined, qualitatively and virtually quantitatively, by the usual wet methods (c.f. DIN 51577). After the combustion the ash content of the sample can also be determined directly from the combustion crucible by simple back-weighing. Some blank tests must be carried out first in order to calibrate out the ash content arising from the combustion agent (e.g. igniter wire). In many cases it is even possible to make a direct analysis of the content of the individual cations (metal ions). These simultaneous analyses are very important, especially with the use of replacement fuels (old tyres, used oil, domestic and special refuse) which are now being used to an increasing extent in cement kilns.

## 7. The adiabatic principle

The water container is placed in a well-insulated calorimeter vessel so that the full combustion heat is measured and as little allowance as possible has to be made for the influence of the surroundings on the measuring system. However, due to the temperature gradient between the inner container and the insulation a certain part of the heat is lost even with the best insulation. Even 20 years ago IKA had developed the first adiabatic calorimeter to eliminate this source of error (Fig. 2). Instead of an insulating jacket, the C 4000 adiabatic

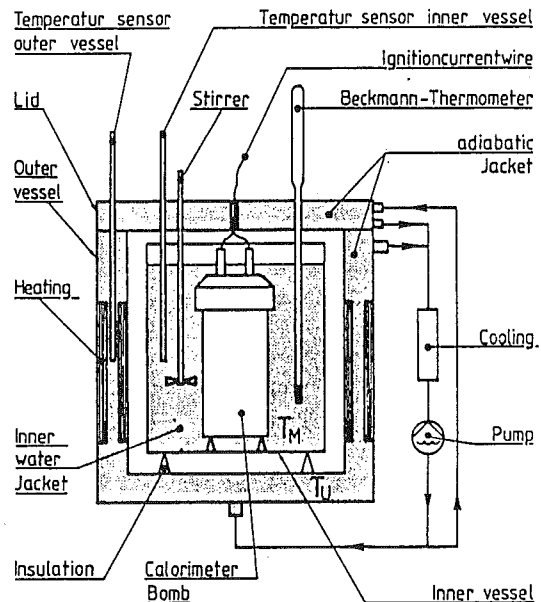


Fig. 2: Bomb calorimeter with adiabatic jacket

calorimeter has an external jacket with integral heating and cooling system. A highly sensitive temperature sensor is placed in the outer jacket, and another in the inner container. This gives the adiabatic calorimeter the advantage over older isothermal systems that, with the aid of its integral heating and cooling system and a sensitive control system, it is possible to balance out even very small temperature differences between the inner and outer containers. If the temperature in the inner container rises, then the heating system heats the outer container to exactly the same temperature. However, when there are no temperature differences between the inner and outer containers the system is adiabatic (i.e. free from heat losses), or, in other words, the insulation is perfect.

### 8. Test sequence in the adiabatic calorimeter

The temperatures before ignition and after the end of the measurement are constant because of the adiabatic principle described. It is therefore only necessary to read off the ignition temperature and the final temperature to be able to calculate the gross calorific value. When the temperature is constant for 3 minutes in the pretest period (Fig. 3) this is recorded as the initial temperature  $T_1$  and the sample in the bomb is ignited automatically. The combustion heat liberated raises the temperature rapidly in the inner container (Fig. 3, main test period). After 8 to 11 minutes the final temperature  $T_2$  is reached.

The gross calorific value  $H_0$  is calculated from these two temperatures:

$$H_0 = \frac{C(T_2 - T_1) - Q_F}{m_p}$$

$C$  = heat capacity of the calorimeter system being used

$Q_F$  = sum of all external quantities of heat which do not arise from the combustion of the substance being investigated (ignition wire, cotton threads, chemical reactions)

$m_p$  = weight of sample

### 9. The C 4000 calorimeter system

The C 4000 system has a modular structure so that the user obtains the equipment configuration of his choice to suit his specific applications. In the final development stage (Fig. 4) the system works fully automatically. The heart of the system is the measuring cell, an adiabatically operating bomb calorimeter which conforms to DIN 51900, ASTM, ISO and other current standards. An integral digital temperature indicator and an integral BCD and V24-RS232 interface makes it possible to link computer systems with the calorimeter. The peripheral equipment has also been perfected and, in particular, the working equipment has been made more user-friendly. The individual system components, such as the calorimeter bomb, filling station, briquetting press, cooling water supply, measuring cell, control, calculation and documentation unit including dot matrix printer, and analytical balance can be seen in Fig. 4.

### 10. Outlook

The new generation of equipment is a continuation of a successful product line and will be used with success in the cement plant of the future. The analysis results – the gross calorific value – will not only be used for settling accounts with the fuel suppliers but also as an additional controlled variable for the combustion process. The fact that this can save costs is certainly a great advantage, but the fact that the ash content, halogen or sulphur content and, under some circumstances, the heavy metal content can be determined from one analysis in addition to the gross calorific value makes the C 4000 calorimeter system an important analytical device for cement, lime and gypsum plants.