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Theoretical energy requirement for burning clinker

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Abstract

Based on studies carried out with two kiln feed samples used for the production of Portland cement, a method for the direct measurement of the theoretical energy requirement (TER) on a high-temperature calorimeter HT 1500 from the company SETARAM (Lyon, France) is presented. Because the use of this method for the determination of the TER presupposes a complete transformation of the raw materials into the respective reaction products, under the conditions prevailing in the calorimeter, additional studies were carried out to verify to what extent the transformation is eventually completed. Based on the results obtained, the influence of the composition of the kiln feeds on the TER is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

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For the calculation of the energy balances of kilns used for burning cement clinker, it is necessary to know, among other factors, the energy consumed for the production of clinker under "ideal" conditions. Because its direct determination was associated with great difficulties, methods were developed, in the past, for its calculation.

With technological developments of recent years in the area of high-temperature calorimetry, methods and equipment were developed that enable the direct determination of the theoretical energy requirement (TER) involved in the production of clinker.

According to Kühl and Knothe [1,2], the TER for burning clinker can be defined as the enthalpy change associated with the isothermal transformation at 293K of a dry kiln feed into the respective reaction products (clinker, carbon dioxide, and water). This process can be described by Eq. (1):

$$(1 + b)\ \text{kg kiln feed } (293K) \rightarrow 1\ \text{kg clinker } (293K) + b\ \text{kg gas } (293K) \qquad \Delta H_1 \qquad (1)$$

where b is the mass in kg of gas (composed mainly of carbon dioxide and water) liberated during reaction, Eq. (1), and ΔH_1 is the TER in kJ/kg clinker.

Because ΔH_1 cannot be measured directly at room temperature, an indirect method was used to determine ΔH_1 with the help of the following data:

1. The enthalpy of the reactions in Eqs. (2) and (3):

   $$(1 + b)\ \text{kg kiln feed } (293K) \rightarrow 1\ \text{kg clinker } (T) + b\ \text{kg gas } (T) \qquad \Delta H_2 \quad (2)$$

   $$1\ \text{kg clinker } (293K) \rightarrow 1\ \text{kg clinker } (T) \qquad \Delta H_3 \quad (3)$$

   where ΔH_2 and ΔH_3 are direct results of the calorimetric measurements,

2. The enthalpy of the transformation given in Eq. (4):

   $$b\ \text{kg gas } (293K) \rightarrow b\ \text{kg gas } (T) \qquad \Delta H_4 \quad (4)$$

   which was determined from data in thermochemical tables [3], and

3. The composition and amount of the gas mixture liberated during reaction, Eq. (1), calculated based on the chemical composition of kiln feed, raw materials, and clinker.

ΔH_1 then can be obtained by linear combination of Eqs. (2), (3), and (4), as given in Eq. (5):

$$\Delta H_1 = \Delta H_2 - (\Delta H_3 + \Delta H_4) \qquad (5)$$

using data given in Eqs. (1), (2), and (3).

For the calorimetric measurements of ΔH_2 and ΔH_3, samples of the kiln feed and clinker were dropped from room temperature into a calorimeter in a thermal stationary state at the measuring temperature $T \approx 1675K$, and the respective thermal effects were measured. The calibration of the calorimeter was made by dropping spheres of platina.

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1. Equipment and methodology

The measurements were made on the HT1500 calorimeter of the company SETARAM (Lyon, France). This equipment is composed basically of two cells arranged vertically, with the upper cell functioning as the measuring cell. To measure the thermal effect taking place in the measuring cell, a thermopile composed of (18 + 18) thermocouples Pt/6Rh-Pt/30Rh is installed around the two cells.

For the calorimetric measurements the following procedure was adopted. After the attainment of a state of thermal equilibration in the calorimeter, a set of four samples of kiln feed or clinker was measured. Alternated with kiln feed or clinker samples, spheres of platina were dropped to calibrate the calorimeter. The masses of the platina spheres were chosen so as to produce thermal effects in the calorimeter similar in magnitude to those of the samples. From the area corresponding to the thermal effect, which was registered and integrated using a computer interfaced with the calorimeter and data from the literature [3], a factor relating the enthalpy effect (in joules) and the respective area of the peak, produced when dropping platina spheres, was determined. This factor was used to determine the enthalpy effect of the samples by multiplying it by the peak area of the samples.

From time to time the calorimeter was checked by measuring corundum (α-Al_2O_3) samples, while calibrating with platina. The values obtained were compared with well-known values for corundum reported in the literature (for example in [3]). More details about the equipment used can be found in references [4] and [5].

2. Sample preparation

From natural limestone, clay, and fly ash raw materials used for the production of the two cements reported here, whose chemical composition is given in Table 1, the following kiln feeds samples were prepared:

Kiln feed I: 76.86% limestone + 23.14% clay

Kiln feed II: 79.43% limestone + 20.57% fly ash.

Table 1
Chemical composition of the raw materials in mass%

Component	Limestone	Clay	Fly ash
C	—	—	1.49
CO_2	42.16	6.63	0.04
H_2O	0.72	6.70	0.40
SiO_2	3.26	45.04	47.82
Al_2O_3	0.70	17.20	27.50
TiO_2	0.06	0.81	1.16
P_2O_5	0.07	0.13	0.14
Fe_2O_3	0.20	8.75	9.88
Mn_2O_3	0.02	0.10	0.25
CaO	52.10	6.47	2.72
MgO	0.38	3.09	2.77
SO_3	0.09	0.37	0.51
K_2O	0.15	3.87	4.74
Na_2O	0.07	0.75	0.63

The chemical composition of the resulting kiln feeds are listed in Table 2.

The raw materials, which were obtained as fine powders, were dried at 393K and proportioned by weight according to composition of kiln feeds I and II. The kiln feed samples obtained were ground/homogenised in a ball mill. After homogenisation, portions of about 20 mg were compressed into small cylinders (ø = 3 mm, h ≈ 2 mm), inserted in capsules made with thin films of platina (10 μm), sealed, and dropped into the calorimeter for measurement of ΔH_2.

For preparation of clinker, kiln feed samples were compressed into cylindrical forms (ø = 19 mm, h ≈ 2 mm) and burnt at ≈ 1675K for 30 min. The product of the reaction was finely ground, compressed into small cylinders, and dropped into the calorimeter. The measured enthalpy effect of these samples represents the enthalpy of the reaction in Eq. (3), ΔH_3.

3. Preliminary experiments

Because the determination of heats of transformation (reaction) using a drop calorimeter presupposes complete transformation of the initial materials (in this case the cement kiln feed) into the respective reaction products within a relatively short period of time (the measuring time here was $\leqslant$10 min), preliminary experiments were carried out to verify if this prerequisite is guaranteed under the conditions prevailing during calorimetric measurements. For this purpose, samples of the homogenised kiln feed were compressed into cylindrical forms (ø = 19 mm, h≈2 mm) and burnt for 10 min at T = 1673K and 1693K for kiln feeds I and II, respectively. The assumption of complete transformation was verified through determination of the free lime content of burnt samples [6].

4. Determination of the factor b

Composition and amount of gas liberated during production of clinker, see Eq. (1), were calculated based on the chemical composition of the raw materials (Table 1) and of the kiln feeds (Table 2).

Table 2
Chemical composition of kiln feeds I and II

Component	Kiln feed I	Kiln feed II
SiO_2	20.23	18.97
Al_2O_3	7.56	10.05
Fe_2O_3	3.41	3.35
CaO	65.03	64.07
MgO	1.58	1.34
SO_3	0.25	0.27
K_2O	1.58	1.67
Na_2O	0.36	0.28

Data are given in mass% and for calcined material.

This determination was hereby carried out (example given is for kiln feed I). Limestone has a loss on ignition of 42.88%, whereas clay has a loss of 13.33%. Because 1 kg of kiln feed contains 0.7686 kg limestone and 0.2314 kg clay, 1 kg of kiln feed will release ($0.4288 \times 0.7686 + 0.1333 \times 0.2314 = 0.36042$) kg of gas. From this relation one can see that, during the production of 1 kg of clinker, 0.5635 kg of gas is released.

5. Results and discussion

The results obtained directly from calorimetric measurements can be summarized as follows:

5.1. Kiln feed sample I

Temp = 1693K
Free lime content = 0.31 mass%
$\Delta H_2' = 2504 \pm 49$ kJ/kg kiln feed ($n = 8$)
$\Delta H_3 = 1465 \pm 28$ kJ/kg clinker ($n = 9$)
$b = 0.5635$ kg gas/kg clinker.

5.2. Kiln feed sample II

Temp = 1703K
Free lime content = 0.50 mass%
$\Delta H_2' = 2360 \pm 37$ kJ/kg kiln feed ($n = 8$)
$\Delta H_3 = 1491 \pm 44$ kJ/kg clinker ($n = 8$)
$b = 0.5257$ kg gas/kg clinker.

ΔH values presented are mean values calculated for n measured data points. The values of $\Delta H_2'$ obtained directly from calorimetric experiments are defined for 1 kg of kiln feed and not 1 kg of clinker, as is the case in Eq. (2). To convert $\Delta H_2'$ into values of ΔH_2, a multiplication by the factor $(1 + b)$ is required, as given in Eq. (6):

$$\Delta H_2 = (1 + b)\Delta H_2'. \qquad (6)$$

ΔH_2 also may be regarded as a TER value, valid only when the final temperature $T \gg T_{room} = 293K$, contrary to the definition in Eq. (1). ΔH_2 is comparable to the definition of the TER normally adopted in the study of technical silicate glasses [4]. The definition of the TER mentioned in [4] considers the transformation of an initial state, represented by a certain amount of kiln feed at room temperature, into a final state, represented by the end products (1 kg of glass melt and respective amount of gases liberated during the process) at a temperature T normally higher than 1300K.

The TER, as defined in Eq. (1), is then calculated using Eq. (7):

$$\Delta H_1 = \Delta H_2 - (\Delta H_3 + \Delta H_4) \qquad (7)$$

where the necessary value of ΔH_4 was calculated from data in reference [3].

The TER values obtained are:

TER ($= \Delta H_1$) of kiln feed I = 1461 kJ/kg clinker

TER ($= \Delta H_1$) of kiln feed II = 1210 kJ/kg clinker.

The substitution of fly ash for clay decreases the TER by about 17%. This decrease of the TER can be explained by the following reasons:

1. Fly ash contains 1.49% coal. The energy liberated during the burning reaction of coal reduces the TER by about 155 kJ/kg clinker.
2. Fly ash is nearly free of hydrates and contains, relative to the clay, fewer carbonates. Hence, during burning of kiln feed II less energy for dissociation of carbonates and hydrates is required.

The results obtained in this study are summarized in Table 3.

To verify the calculation procedure proposed in reference [2], we obtained for kiln feed sample I a ΔH_1 value of about 2100 kJ/kg. This calculation was not carried out for kiln feed sample II, because fly ash is predominantly a vitreous material (metastable material) whose thermodynamic state cannot be exactly defined.

Because of the large deviation observed, we made some attempts to calculate a better estimate of ΔH_1. Here we considered two steps:

1. The dissociation of the raw materials (limestone and clay) into their respective oxides. Whereas limestone was treated as pure calcium carbonate, the mineralogical composition of the clay was determined using a normative method described in reference [7].
2. The formation of clinker phases from the oxides obtained in the dissociation of the raw materials.

The phase composition of the clinker was determined using a normative procedure based on the previous determination of the alumina moduli and the lime saturation factor [8]. This method was developed for calculation of the potential phase composition of the clinker when its chemical composition is known.

The thermodynamic data used in the calculation were taken basically from reference [3]. Additional data, not listed in [3], were obtained from references [9] and [10]. ΔH_1 then was calculated using Hess' law as a sum of the heat of dissociation of the raw materials into their respective oxides and the heat of formation from oxides of the clinker phases. Although the value of ΔH_1 we obtained for kiln feed I ($\Delta H_1 = 1607$ kJ/kg clinker) is better than the one obtained

Table 3
Enthalpy effects of reactions (1) to (4)

	Kiln feed I (T = 1693K)	Kiln feed II (T = 1703K)
ΔH_2 from Eq. (2)	3915	3600
ΔH_3 from Eq. (3)	1465	1491
ΔH_4 from Eq. (4)	989	899
ΔH_1 from Eq. (1)	1461	1210

Data are given in kJ/kg clinker.

using the procedure described in reference [2], it shows still a relatively large deviation from the experimental value (ΔH_1 = 1461 kJ/kg clinker).

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