

## Chapter 2

# Portland Cement Clinker

### 2.1 Portland Cement Clinker Burning

The main goal of the clinkering process is to produce the material of designed phase composition, which is called Portland cement clinker. Under the action of high temperature, parallel to the clinker phases formation, underwent the process of sintering and nodulization of material in the rotary kiln. It is of high technological importance, having the decisive influence on the rate of material transport and also on the quantity of dust carry off with gases in the kiln and in the cooler, then having its effect on heat consumption and kiln capacity.

Raw mix, composed of limestone, marl and small addition of iron corrective component is transformed, as the effect of several complicated reactions, in clinker containing from 55 to 65 %  $C_3S$ , 15–25 %  $C_2S$ , 8–12 %  $C_3A$  and 8–12 %  $C_2(A, F)$ .

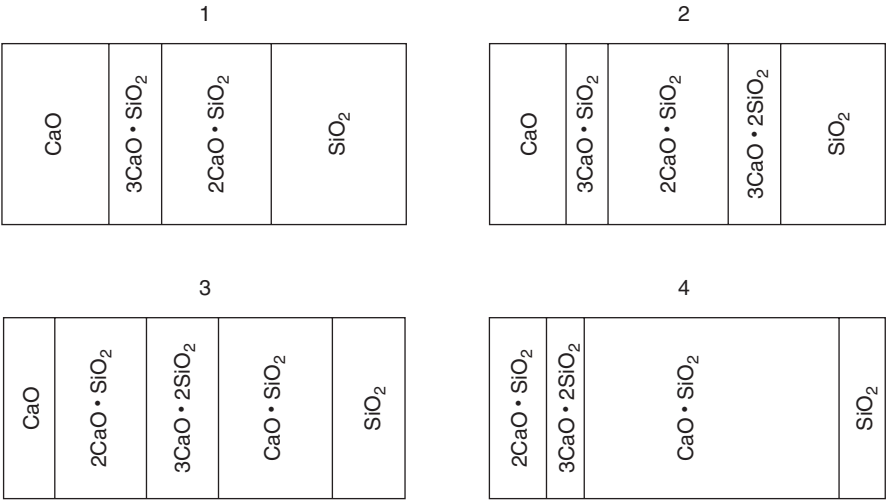
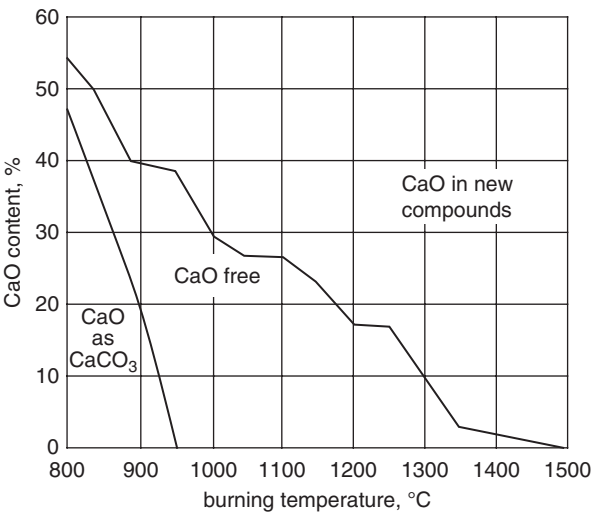
It is convenient to follow the advancement of clinkering process by determining the free calcium oxide in the raw mix, called frequently “free lime”. The content of this component on the beginning is increasing quickly, as a result of calcium carbonate decomposition, and then is gradually decreasing (Fig. 2.1), as the new compounds are formed with silica, alumina and iron.

In the process formation two stages can be distinguish: at the range of lower temperature to about 1300 °C, when the reactions proceed, as a rule, in the solid state, in the presence of very low quantities of the liquid phase, and at higher temperature, at which it is already about 25 % of the melt. It is assumed that the dicalcium silicate<sup>1</sup> and calcium aluminate and ferrite are formed principally as the result of reactions in the solid state. However, tricalcium silicate is formed by crystallization from the liquid phase.

The solid state reactions of  $CaCO_3$  with  $SiO_2$ ,  $Al_2O_3$  and  $Fe_2O_3$  was the object of numerous, systematic studies [1–4]. They belong to the reactions of solid phases with the formation of products interlayer between substrates. In the case of pressed sandwiches of  $CaO$  and silica as the first product the  $2CaO \cdot SiO_2$  is formed and then—in  $CaO$  tablet— $3CaO \cdot SiO_2$  and in the  $SiO_2$  tablet—rankinite  $3CaO \cdot 2SiO_2$

<sup>1</sup>Dicalcium silicate is the orthosilicate with formula  $Ca_2[SiO_4]$ , and tricalcium silicate—orthosilicate with formula  $Ca_3[SiO_4]O$ .

**Fig. 2.1** Combination of lime during raw mix clinkering



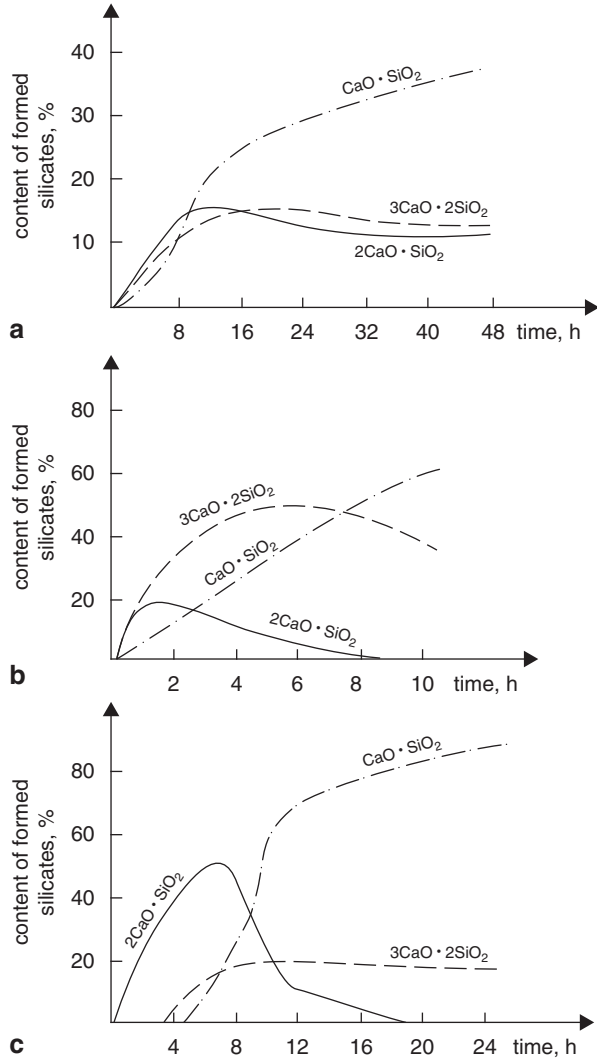
**Fig. 2.2** The sequence of phases formation during the reaction of CaO with SiO<sub>2</sub> with molar ratio of substrates 1:1, 1–4 increase of the reaction time

(Fig. 2.2.). The change of products phase composition of the reaction versus time are shown in Fig. 2.3 [3].

The kinetic of this reaction was studied by Jander [3], which assumed that its rate is governing by the diffusion of one substrate (CaO) through the layer of the product formed to the surface of second substrate (SiO<sub>2</sub>). Under different simplifying assumptions, using first Fick’s law, Jander derived the formula

$$y^2 = kt \tag{2.1}$$

**Fig. 2.3** The content of products in the function of CaO with SiO<sub>2</sub> reaction time in the mixture with molar ratio 1:1 (after [3]); **a** in dry air at 1000 °C, **b** in moist air at 1000 °C, **c** in dry air at 1200 °C

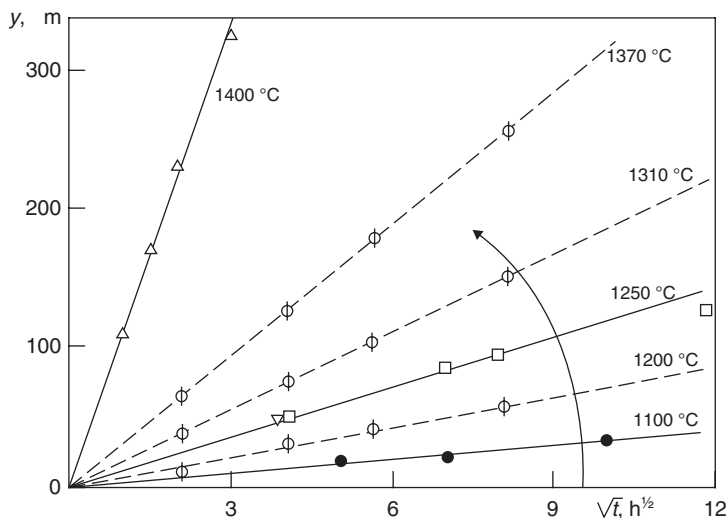


in which  $y$  was the product layer thickness,  $k$ —rate constant,  $t$ —time.

The layer thickness can be easily replaced by degree of transformation:

$$\alpha = \frac{\frac{4}{3}\pi r^3 - \frac{4}{3}\pi(r-y)^3}{\frac{4}{3}\pi r^3} \quad (2.2)$$

where  $r$  is the radius of substrate grain ( $\text{SiO}_2$ ), covered with product layer. After introducing to the proceeding formula the expression is given



**Fig. 2.4** The rate of product layer growing in relation to heating time in the mixtures:  $\text{CaO} + \text{SiO}_2$ —full line and  $\text{CaO} + \text{Al}_2\text{O}_3$ —broken line (diagrammatic)

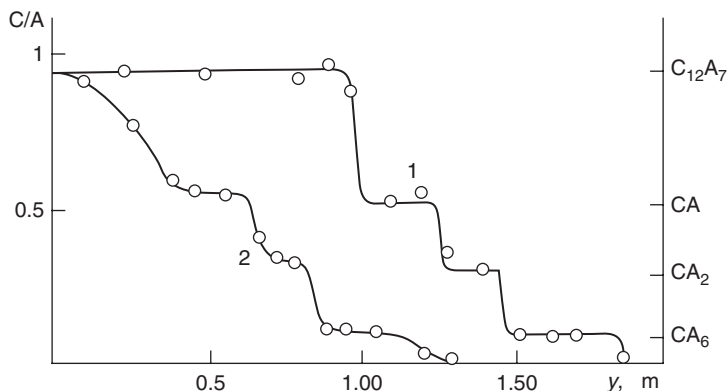
$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = \left[k / r^2\right] t \quad (2.3)$$

in which  $\alpha$  is the degree of transformation after time  $t$ ,  $k$ —rate constant,  $r$ —radius of reacting grains.

The degree of transformation can be followed by free calcium oxide determination in the raw mixture. The experimental results for different time of reaction, put on the diagram of relation  $\left[1 - (1 - \alpha)^{1/3}\right]^2$  for time give the straight lines, which coefficient of inclination is increasing with temperature.

Weisweiler et al. [5] studied the reaction advancement on the frontier of two tightly bordered tablets of  $\text{CaO}$  and  $\text{SiO}_2$ , prepared by hot pressing. Samples heated at the temperature range  $1000\text{--}1450^\circ\text{C}$  gave the analogous to earlier established products sequence. However, simultaneously the glass formation of the approximate formula “ $\text{CS}_2$ ” was found, at the temperature higher than  $1300^\circ\text{C}$ . The product layers have thus the sequence:  $\text{C}/\text{C}_2\text{S}/\text{CS}/\text{“CS}_2\text{”}/\text{S}$ . The glass is formed as a result of calcium diffusion to the lattice of cristobalite or tridymite, in connection with polymorphic transformation of  $\text{SiO}_2$ . The rate of multiphase layer growing ( $y$ ) in the function of reaction time ( $t$ ) is well described by the Jander’s formula  $y^2 = kt$  (Fig. 2.4). Deja [6] researching the influence of different calcium silicates on the rate of tricalcium silicate formation found that it is the highest in the case of  $\text{C}_2\text{S}$ , and the slowest, when one of the substrate is a chain silicate.

Also in the case two-components mixtures, calcium carbonate or oxide with iron (III) oxide, in which ferrite are formed, and three components mix:  $\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , in which alumina-ferrites are formed, Jander’s formula is well satisfied.



**Fig. 2.5** Phase composition of reaction zone in corundum pulley [(after 9)]; 1 pulley heated in powdered CaO at 1370 °C, 2 pulley heated second time at the same temperature after removing CaO

First aluminate formed in the mixture  $\text{CaO} + \text{Al}_2\text{O}_3$  is the monocalcium aluminate  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ . At the temperature about 900 °C  $\text{C}_{12}\text{A}_7$  appears, which is transformed in  $\text{C}_3\text{A}$  at the temperature higher than 1200 °C, in practice close to 1300 °C. The studies of reaction rate in the mixture  $\text{CaO} + \text{Al}_2\text{O}_3$  with molar ratio 3:1, in which  $\text{Ca}_3\text{Al}_2\text{O}_6$  is the final product, have shown that the Ginstling–Brounsteins’ [7] formula is better fulfilled than Jander’s equation:

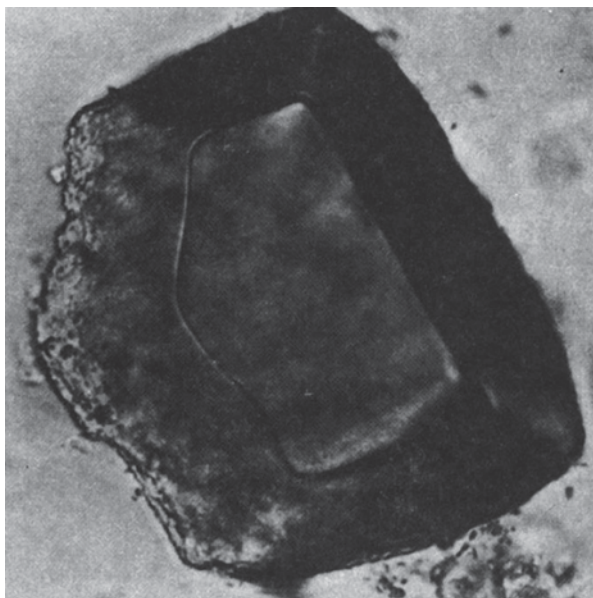
$$\frac{(1 - 2\alpha)}{[3 - (1 - \alpha)^{2/3}]} = (k / r^2)t \quad (2.4)$$

Also in the case of this mixture the interpretation of the results is complicated, because apart of  $\text{C}_3\text{A}$  other phases appear among the products, namely: CA,  $\text{C}_{12}\text{A}_7$ ,  $\text{CA}_2$  and even  $\text{CA}_6$ . This complicated phase composition of reacting mixture is showing that the mobile component is CaO and the product layers onto  $\text{Al}_2\text{O}_3$  grains are formed.

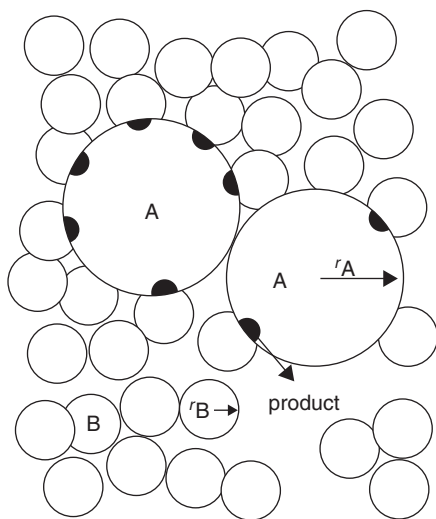
The mechanism of reaction in the solid state of the mixtures CaO with  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  was studied by many authors and all have confirmed the much higher mobility of the calcium ions than the others [5, 8, 9]. Also Rouanet [9], studying the phase composition of the reaction layer, formed in the corundum pulley immersed in powdered CaO, showed in Fig. 2.5 confirmed it. However, the XRD examination of the powder around the  $\text{Al}_2\text{O}_3$  pulley, has shown the presence of thin layer of  $\text{C}_3\text{A}$ , which confirms the alumina ions diffusion in the opposite direction to calcium ions [9].

For the reason of low diffusion coefficients of silicon and aluminium the rate of reaction is determined by the calcium ions diffusion and oxygen, the last probably through the gaseous phase. Such mechanism of this process is confirmed by frequently observed in industrial mixtures the thin layers of  $\text{Ca}_2[\text{SiO}_4]$  on quartz grains. On the Fig. 2.6 this layer, found by Moore [(after 10)], is shown in the specimen of the material sampled in industrial rotary kiln.

**Fig. 2.6** The layer of  $C_2S$  on quartz grain. (After [10])



**Fig. 2.7** The Komatsu's model of reaction in the solid state



The kinetic models of Jander and Ginstling were developed by Komatsu [11]. He had assumed that the reaction starts in the places of intergranular contact (Fig. 2.7). The fundamental role in the reaction has the number of these contacts, thus the fineness of the mixture. If the number of contacts is constant in time, the formula derived by Komatsu is reduced to Jander's equation, in which, however, the  $k$  constant is the function not only of the temperature but also the ratio of grains sizes  $r_A$  and  $r_B$  of both components as well as the content ratio of these components in the mixture.

The equations of reaction constant rate between the substrates A and B are the following:

when  $A/B > 1$

$$k = k_0 \left[ \frac{ax}{1+ax} \right]^{m_1} \quad (2.5)$$

when  $A/B < 1$

$$k = k_0 \left[ \frac{1}{1+ax} \right]^{m_2} \quad (2.6)$$

where:— $A/B$  is the molar ratio of the substrates in the mixtures,  $a = r_B^3 \rho_B / (r_A^3 \rho_A)$ —mass ratio of single grain B to the grain A:  $r_A$ ,  $r_B$ ,  $\rho_A$ ,  $\rho_B$ —grains diameters and densities of the components A and B,  $x$ —mass ratio of component A to the mass of component B.

The experimental results in the coordinate system  $\log k - \log[ax/(1+ax)]$  and  $\log k - \log[1/(1+ax)]$  should lay on two straight lines of inclination equal  $m_1$  and  $m_2$ . Both lines should intersect in point  $k_0$  if the mechanism of reaction is the same for both concentration ranges. Practical application of Komatsu's equation can be found in the paper of Haber and Ziółkowski [12].

From kinetic reason the composition of reacting mixtures is frequently very complicated and far from equilibrium. It should be reminded that the thermodynamic permits to determine the equilibrium phase composition of reaction mixture: this state has the lowest free enthalpy. This principle permits to find *a priori* the direction of reaction course or permits to determine the phases stability in determined thermodynamic conditions. The change of free enthalpy can be found from the Gibbs–Helmholtz's equation [13]:

$$\Delta G_T^0 = \Delta H_{298}^0 - T \Delta S_{298}^0 + \int_{298}^T \Delta C_p \quad (2.7)$$

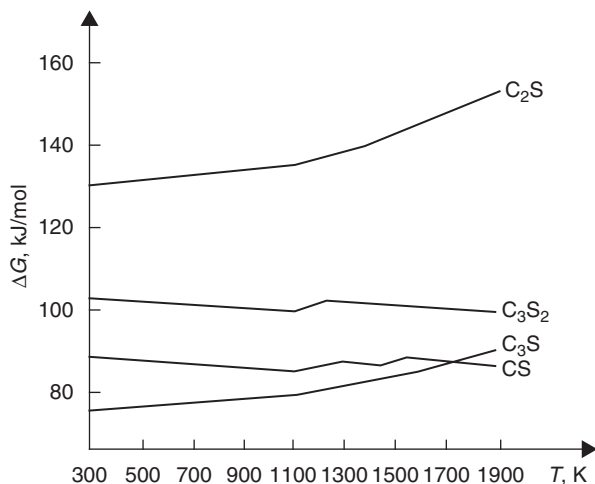
The standard enthalpy data ( $\Delta H_{298}^0$ ), standard entropy ( $S_{298}^0$ ) and molal heat capacity ( $C_p$ ) of substrates and products can be found in the tables [13] or on the Internet. Their changes as the result of reaction can be calculated as the sum of enthalpy (entropy) of products diminished by the sum of enthalpy (entropy) of substrates:

$$\Delta H_{298}^0 = \sum \Delta H_{298}^0 \text{ (of products)} - \sum \Delta H_{298}^0 \text{ (of substrates)} \quad (2.8)$$

If there is no molal heat capacity as a function of temperature we can use the simplified formula:  $C_p = a + bT + cT^{-2}$ . The example of calculated values for the mixture  $2\text{CaO} + \text{SiO}_2$  is shown in Fig. 2.8 [13]. However, the lack of some precise thermodynamic data is for the present the limitation of this method.

The reaction kinetic of models mixtures, of the composition close to industrial one and at the temperature corresponding to the real production processes, thus in

**Fig. 2.8**  $\Delta G^0$  of the reaction of CaO with  $\text{SiO}_2$  in the function of temperature for the mixture  $2\text{CaO} + \text{SiO}_2$ . (After [13])



the case of important content of liquid phase, was also studied. The liquid phase plays the main role in the formation process of tricalcium silicate. Kondo and Choi [14] have shown that the rate of  $\text{CaO}$  and  $\text{Ca}_2[\text{SiO}_4]$  dissolution in the melt and crystallization of  $\text{Ca}_3[\text{SiO}_4]\text{O}$  can be presented with the relation analogical to Jander's formula, in which the volumetric diffusion in the solid state was replaced by dissolution. It is as follows:

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = \frac{2D\Delta c}{r^2} t = kt \quad (2.9)$$

In this equation  $D$  is the diffusion coefficient,  $\Delta c$ —the concentration difference in diffusion layer,  $r$ —the radius of dissolving grains, and the remaining symbols as in Jander's equation.

The diffusion coefficient can be calculated from the equation:

$$D = \frac{RT}{6\pi\eta\delta N} \quad (2.10)$$

where:  $\eta$ —melt viscosity,  $\delta$ —the radius of the particles under diffusion (the authors adopted 40 pm for  $\text{Si}^{4+}$ ),  $R$ —gas constant,  $T$ —temperature,  $N$ —Avogadro's constant.

The simple formula for the calculation of free CaO in the clinkering process by Johansen [15] was given; he admitted that the limiting of the process rate factor is diffusion:

$$(1 + \beta\alpha)^{2/3} - \frac{2}{3}\alpha = 1 - \left[ \frac{2\gamma D\Delta c}{d_1} \right] \left[ \frac{t}{r_0^2} \right] \quad (2.11)$$

where:  $\alpha$ —is the degree of CaO transformation,  $\beta$ —coefficient dependent of sample composition and porosity,  $\gamma$ —volume fraction of liquid phase content in surface layer of the tablet,  $D$ —effective, two-dimensional coefficient of CaO diffusion,  $\Delta c$ —CaO concentration gradient in the reaction layer,  $d_1$ —density of CaO,  $t$ —time,  $r_0$ —the radius of CaO grains.

Applying this model Johansen calculated that at temperature of 1500 °C and heating time of 20 min the CaO grains of 80  $\mu\text{m}$  diameter will react, which are corresponding to calcite grains equal 120  $\mu\text{m}$ . It is in accordance with earlier Heilmann [16] research. On the base of experiments with the sandwiches ( $\text{C}+\text{C}_3\text{S}$ ) and ( $\text{C}_3\text{S}+\text{C}_2\text{S}$ ) Johansen and Christensen [17] applied the simpler formula, which gives the possibility to eliminate the grains diameter. The formula is:

$$x^2 = kt \quad (2.12)$$

simultaneously

$$k = 2D_m\beta cH \quad (2.13)$$

and

$$H = \frac{1}{C_1 - C_a} + \frac{1}{C_b - C_2} \quad (2.14)$$

In these formula  $x$  is the layer thickness of  $\text{C}_3\text{S}+\text{C}+\text{melt}$  or  $\text{C}_3\text{S}+\text{C}_2\text{S}+\text{melt}$ ,  $k$ —rate constant,  $t$ —time,  $D_m$ —effective, two-dimensional coefficient of CaO diffusion, with the simultaneous diffusion  $\text{SiO}_2+\text{Al}_2\text{O}_3$  etc. in opposite direction, in the melt,  $\beta$ —mass content of the melt in the  $\text{C}_3\text{S}$  layer,  $\Delta c$ —concentration difference of CaO (mass fraction) in the melt in equilibrium with  $\text{C}_3\text{S}+\text{C}$  or  $\text{C}_2\text{S}+\text{C}_3\text{S}$ ,  $C_1$ ,  $C_2$ —mass shares CaO in two,  $C_a$ ,  $C_b$ —mass shares of CaO in  $\text{C}_3\text{S}$  layer on the surface of sandwich I– $\text{C}_3\text{S}$  and of sandwich II– $\text{C}_3\text{S}$ .

The sequence of phases appearing in the mixtures composed of natural raw materials was also examined. In the mixture of calcium carbonate with quartz and clay minerals first reactions are the dehydroxylation of the latters. The kaolinite dehydroxylation at the temperature close to 450 °C is transforming in metakaolinite, which has, in disturbed form, the structure of initial mineral [18]. It is presenting high reactivity with calcium carbonate and the reaction of these components will start at this range of temperatures. For these reasons the mixture of marl with kaolinite produce  $\text{C}_3\text{S}$  at 1100 °C and with illite even at 1000 °C [19].

The calcium carbonate starts to react with quartz at temperatures close to 600 °C, and it is probably linked with the increase of  $\text{SiO}_2$  reactivity, caused by its polymorphic transformation at 573 °C. It is so called Hedvall's effect [20]. As the first phase calcium disilicate is formed. At the almost the same temperature the mono-calcium aluminate and ferrite  $\text{Ca}_2[\text{Fe}_2\text{O}_5]$  will be formed. Some authors mention the CF appearing [21].

At the temperature range 600–700 °C the decarbonisation of calcium carbonate is beginning too. The reaction rate very low at the temperatures from 600 to 800 °C,

is gradually increasing, and many experimental works have confirmed the validity of Arrhenius equation [22]:

$$k = A \exp \frac{-E_a}{RT} \quad (2.15)$$

where:  $k$ —reaction rate constant,  $E_a$ —apparent activation energy,  $R$ —gas constant,  $T$ —absolute temperature,  $A$ —constant (lattice elements oscillation frequency).

During the reaction in the solid state the decomposition processes and polymorphic transformations of mineral components, which cause the lowering of apparent activation energy of reaction, are very important. The processes of clay minerals dehydroxylation, calcium carbonate decomposition, which cause the formation of phases *in statu nascendi*, frequently amorphous with different structural disorganisations, belong to them. For this primarily reason the rate of temperature rise is important. Low rate of heating, favouring the processes of crystallization and recrystallization, the decrease of reactivity of these phases is causing, for example of calcium oxide, formed of  $\text{CaCO}_3$  decarbonisation, which causes the general rate decrease of clinkering process.

The aluminate  $\text{C}_{12}\text{A}_7$  begins to appear at the temperature 800–1000 °C, which then is transformed in  $\text{C}_3\text{A}$  at the temperature range 1000–1200 °C. It should be underlined that in practise the large differences of temperature of individual phases appearing can be observed, which is understandable if the numerous changeable factors influencing these heterogeneous processes will be considered. There are principally: grains sizes, degree of raw meal homogenisation and presence of impurities. On Fig. 2.9 the ranges of different phases appearance, according to the literature, are presented.

Gehlenite is an intermediate phase formed at the temperature range of 800–1200 °C by some authors is mentioned. Starting from the temperature 950–1000 °C the formation of ferrites  $\text{C}_2(\text{A}, \text{F})$  can be observed.

The mixtures of natural raw materials contain always low quantity of alkalis, sulphates and chlorides, which eutectics of melting temperature lower than 700 °C is formed [23]. The liquid phase formation highly increases the rate of reactions, accelerating diffusion of several orders of magnitude. Higher amounts of liquid phase start to appear at the temperature of about 1200 °C and are linked with the eutectic  $\text{CF}-\text{CF}_2$ , and then at about 1280 °C. The last one corresponds to eutectic  $\text{C}_2\text{S}-\text{C}_{12}\text{A}_7-\text{C}_2(\text{A}, \text{F})$ . Clinker's melt is corresponding to the invariable point  $\text{C}_3\text{S}-\text{C}_2\text{S}-\text{C}_3\text{A}-\text{C}_4\text{AF}$ , thus with the phases richer in lime, but poorer in alumina, which melting temperature is 1338 °C.  $\text{MgO}$  and  $\text{R}_2\text{O}$  lower the appearing of the liquid phase to 1260 °C [24].

The content of clinker melt is increasing with temperature, and its viscosity is decreasing. The content of liquid phase at chosen temperature (compare with Sect. 2.2) can be calculated from corresponding multicomponent systems. Lea and Parker [24] gave the simplified formulae, which permit the content of liquid phase calculation:

- liquid phase content at 1340 °C =  $6.1y + a + b$  (for  $\text{A/F} > 1.38$ )
- liquid phase content at 1340 °C =  $8.5x - 5.22y + a + b$  (for  $\text{A/F} < 1.38$ )
- liquid phase content at 1400 °C =  $2.95x + 2.2y + a + b$
- liquid phase content at 1450 °C =  $3.0x + 2.25y + a + b$



<http://www.springer.com/978-94-007-7944-0>

Cement and Concrete Chemistry

Kurdowski, W.

2014, XII, 700 p. 477 illus., Hardcover

ISBN: 978-94-007-7944-0