

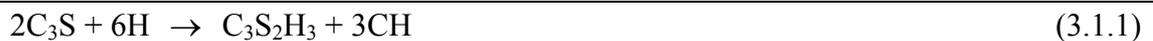
3. PHYSICOCHEMICAL CHARACTERISTICS

3.1 Review of cementitious and pozzolanic reactions

3.1.1 Portland clinker hydration

Portland clinker consists essentially of crystalline compounds of calcium combined with silica, alumina, iron oxides, and sulphates. Typically, the approximate composition (including calcium sulphate) and amounts of the principal minerals present are: C₃S: 50%, C₂S: 25%, C₃A: 10%, C₄AF: 8% and gypsum C \bar{S} H₂: 5% (the notation of cement technology is used- *see Notation*).

Although the chemical reactions of *hydration of portland clinker compounds* are complex and do not proceed to completion, a *simplistic view* of the chemistry of the principal setting and hardening reactions may be presented in terms of chemical reactions. As regard the *hydration reactions of C₃S and C₂S*, many authors have agreed upon the following scheme [9,11,22-27]:

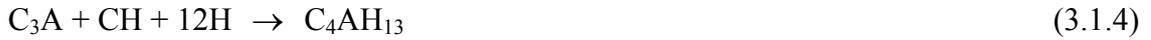


It must be emphasized that the formula given for C₃S₂H₃ (C-S-H, calcium silicate hydrate) is only a very rough approximation, since not only is a material actually non-stoichiometric and very poorly crystalline, but also more than one variety of C-S-H is formed during hydration.

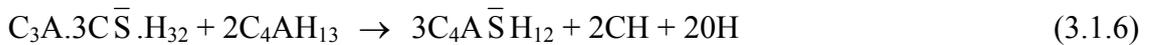
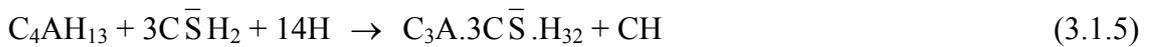
For the hydration of the other phases, C₃A and C₄AF, there is a vague image in the literature. In the case of *C₃A hydration*, Bensted [22] and Frigione [23] presented a satisfactory reaction scheme. In a system *without lime and gypsum* the reaction is the following:



However, when lime is present (in the absence of gypsum), the C_3A hydration is described by:



This reaction is the principal cause of *flash set* in portland clinker, and in order to prevent it, gypsum is added to the clinker. When both lime and gypsum ($C\bar{S}H_2$) are present, as in the real case of cement hydration, in addition to Eq. (3.1.4) the following reactions take place:



As observed, C_3A begins its rapid reaction with lime and water to form calcium aluminate hydrate (C_4AH_{13}). There *immediately* follows a reaction between calcium sulphate in solution and the calcium aluminate hydrate to form ettringite ($C_3A.3C\bar{S}.H_{32}$, an insoluble compound that is deposited on the surface of the hydrating C_3A , providing an effective barrier against further rapid hydration). However, in a very short time ettringite reacts with calcium aluminate hydrate to form the more stable phase of monosulphate ($C_4A\bar{S}H_{12}$). When all the gypsum is used up, C_4AH_{13} continues to be formed from any remaining unhydrated C_3A and the final product is a monosulphate- C_4AH_{13} solid solution. If there is excess of gypsum then the main product is the monosulphate. By adding the Eq. (3.1.4)-(3.1.6), the overall equation of monosulphate formation is obtained:



C_4AF , actually a solid solution within the C_2A - C_2F system, reacts at a slower rate than C_3A and forms iron (III) analogs of ettringite, monosulphate and calcium aluminate hydrate. However, when such reactions are used for calculations, an overestimation of water-bound content is observed. Therefore, a reaction that binds less water should take place. According to Frigione [23], gypsum (SO_4^{2-} ions) reacts preferentially with C_3A rather than C_4AF . In this case, practically in the absence of gypsum, the C_4AF hydration may be described by the following equation [27]:



The main product of clinker hydration is the *calcium silicate hydrate* (*C-S-H* or *CSH*), which is highly cementitious and constitutes about 60-65% of the total solids in a fully hydrated portland clinker. *Calcium hydroxide* (*CH*) is the second product of hydration (about 20%). It contributes little to the cementitious properties of the system, but offers the alkaline environment for the steel passivation. The remaining hydration products (about 15-20%) consist of calcium monosulphate aluminate hydrate and its iron analog, and calcium aluminate hydrate and its iron analog, and are capable of contributing strength to hardened cement paste.

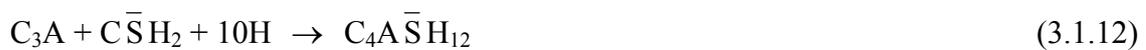
3.1.2 Pozzolan reactions

Supplementary cementing materials (*SCM*) are composed of the same oxides as portland clinker, but in different proportions and mineralogical compositions. As defined earlier, the reaction of these materials with $Ca(OH)_2$ (lime) is called *pozzolanic reaction*. Not all siliceous and aluminous materials are pozzolanic. It is known that crystalline minerals, e.g., silica as quartz, alumina as corundum, and aluminosilicates such as sillimanite (S.A) and mullite (3S.2A) *do not react* with lime solution at room temperature. *It is only when the siliceous and aluminous materials are present in non-crystalline (amorphous, glass) form and as fine particles, which they can hydrate at a slow rate in alkaline solutions.* This is *contrary to the hydration conditions in portland clinker* where the principal compounds are essentially crystalline, but decompose rapidly in water to provide the desired ions for formation of the cementitious hydrates. Therefore, it should be emphasized that the *mineralogical composition (glass phase content) and particle size* rather than the chemical composition would determine whether or not, or how fast a material can react with lime.

Particular attention should then be paid to *the nature of the possible reactants* in the pozzolans, and especially to glass content and type. As mentioned above, the crystalline materials are not active. An exception to this is high-calcium fly ash containing crystalline materials, such as C_3A and $C_4A_3\bar{S}$, which are reactive. Typically, fly ash contains 60-90% glass, granulated slags contain 85-95% glass, and condensed silica fume consists essentially

of vitrified silica (almost 100% glass). The characteristics of the glassy phase in siliceous by-products, which range from simple (silica fume) to highly complex (fly ash) are reviewed elsewhere [15,28]. The “pozzolanic activity” is not limited to the lime-silica interaction, but includes all pozzolanic and cementitious reactions in the system: CaO-SiO₂-Al₂O₃-Fe₂O₃-SO₃-H₂O. It is accepted [14,17,29], that the difference between the “pozzolanic reactions” and portland clinker hydration reactions lies mainly in the reactants and the reaction rates, and not in the character of the hydration products. The *relative rates* of hydration of SCM depend, in general, on particle size and the composition of the non-crystalline phase. The reason for the slow reactivity is the mechanism of hydration according to which the particles hydrate essentially in situ by diffusion-controlled reactions. This is why particle size or surface area plays a dominant role in determining the relative rates of reactivity.

Knowing the reactants and the final products, and ignoring the intermediate steps, Papadakis et al. [30] were the first to propose a simplified scheme describing pozzolanic activity in terms of chemical reactions, but without an experimental verification. Later, Papadakis [31-34] developed a more reliable scheme for pozzolanic reactions with extended experimental verification. According to that analysis, the most plausible simplified equations, which can describe the pozzolanic activity of a *complex SCM* (containing active silica, alumina and calcium), are summarized as follows:



All this scheme describes sufficiently the cases when the SCM is *calcareous fly ash, blast furnace slag or similar SCM*. In the case when the SCM is *silica fume*, the Eq. (3.1.9) is the only valid. In the case when the SCM is *siliceous fly ash*, the Eqs. (3.1.9)-(3.1.11) are almost the only valid. The reaction (3.1.10), which dominates in high-gypsum systems, takes place *through several intermediate steps* including reaction (3.1.11), ettringite formation and its conversion to monosulphate.

3.2 Quantification of final products and pore volume

The portland clinker and the SCM can be easily analyzed in terms of oxides: total CaO (C), free CaO (Cf), SiO₂ (S), Al₂O₃ (A), Fe₂O₃ (F), SO₃ (\bar{S}), and other oxides, filler, or impurities denoted all by R. Let us denote then as $f_{i,K}$ and $f_{i,P}$ the weight fractions of the constituent i ($i=C, Cf, S, A, F, \bar{S}, R$) in the portland clinker and SCM, respectively. We assume that *mac* is almost filler without a significant participation in the chemical reactions. We denote herein as “portland cement” the sum of portland clinker, additives, and calcium sulphate, i.e., everything but cement’s SCM and *mac*.

As mentioned in the previous sections not all of the total mass of the oxide i in an SCM is active (only the glass phase; with the exception of high-Ca SCM where some crystalline phases are also active). Let us denote by $\gamma_{i,P}$ the weight fraction of the oxide i in the SCM, which contributes to the pozzolanic reactions (“activity” ratio).

Taking into account the cement composition presented in section 2, the clinker content in concrete, \mathbf{K} (kg/m³ of concrete), the cement’s SCM content in concrete, \mathbf{P} (kg/m³ of concrete), the *mac* content in concrete, \mathbf{MAC} (kg/m³ of concrete), and the calcium sulphate content in concrete, \mathbf{CS} (kg/m³ of concrete), are given respectively by:

$$\mathbf{K} = (p_K/100) C (100-p_{CS})/100 \quad (3.2.1)$$

$$\mathbf{P} = (p_{SCM}/100) C (100-p_{CS})/100 \quad (3.2.2)$$

$$\mathbf{MAC} = (p_{MAC}/100) C (100-p_{CS})/100 \quad (3.2.3)$$

$$\mathbf{CS} = (p_{CS}/100) C \quad (3.2.4)$$

From the point of view of reinforcement protection, as well as for the completion of the pozzolanic activity, the quantity of calcium hydroxide, Ca(OH)₂, plays a dominant role (see carbonation chapter). The quantity of calcium-silicate-hydrate, C₃S₂H₃, is the main strength-bearing component in the hydrated cement (see strength chapter). The chemically-bound water, H , defines the minimum required water content for complete hydration of the cementitious materials. The concrete porosity, i.e., the ratio of total void volume to total concrete volume, plays a significant role in the propagation of the deterioration phenomena

[9-11]. In the sequence, and according to cement and addition type used, we distinguish the following separate cases for examination.

3.2.1 Cement type CEM I

a. Cement type CEM I without concrete additions

The weight fractions of the various phases (C_3S , C_2S , C_3A , C_4AF , $C\bar{S}H_2$) in portland clinker can be determined from the oxide analysis using Bogue's formulas [26,35]:

$$C_3S = 4.071(f_{C,K} - f_{Cf,K} - 0.7f_{\bar{S},K}) - (7.60f_{S,K} + 6.72f_{A,K} + 1.43f_{F,K}) \quad (3.2.5)$$

$$C_2S = 2.867f_{S,K} - 0.754(C_3S) \quad (3.2.6)$$

$$C_3A = 2.65f_{A,K} - 1.692f_{F,K} \quad (3.2.7)$$

$$C_4AF = 3.043f_{F,K} \quad (3.2.8)$$

The *portland clinker hydration reactions in presence of calcium sulphate (gypsum)* have been presented in section 3.1.1, and with an excess of gypsum, Eq. (3.1.1), (3.1.2), (3.1.7) and (3.1.8) are dominant. This is valid when $C\bar{S}H_2 > 0.637C_3A$; as applies typically when p_{CS} is about 5%. Using the stoichiometry of these reactions and the molar weights of the reactants and products (given in Table 3.2.1), *the amounts of the finally produced compounds* can be estimated. The Eq. (3.2.5)-(3.2.8) can be used to express these amounts as a function of the oxide contents in clinker. Thus, the amounts of CH, $C_3S_2H_3$ (CSH), $C_4A\bar{S}H_{12}$ ($CA\bar{S}H$), C_6AFH_{12} (CAFH), and chemically bound water (H) are given as follows, in kg/m^3 of concrete [11,31]:

CH	=	$\{1.321(f_{C,K} - 0.7f_{\bar{S},K}) - (1.851f_{S,K} + 2.182f_{A,K} + 1.392f_{F,K})\} K$	(3.2.9)
CSH	=	$2.85f_{S,K} K$	(3.2.10)
$CA\bar{S}H$	=	$(6.106f_{A,K} - 3.898f_{F,K}) K$	(3.2.11)
CAFH	=	$5.099f_{F,K} K$	(3.2.12)
H	=	$\{0.321(f_{C,K} - 0.7f_{\bar{S},K}) + 1.236f_{A,K} - 0.113f_{F,K}\} K$	(3.2.13)

Table 3.2.1 Molar weights and volumes of the main compounds found in portland cement and portland cement-based binders*

Compound	Molar weight x10 ³ (kg/gmol)	Density x 10 ⁻³ (kg/m ³)	Molar volume x10 ⁶ (m ³ /gmol)
C ₃ S	228.30	3.20	71.34
C ₂ S	172.22	3.30	52.19
C ₃ A	270.18	3.03	89.17
C ₄ AF	485.96	3.77	128.90
C \bar{S} H ₂	172.17	2.32	74.21
H	18.02	1.00	18.02
CH	74.10	2.24	33.08
C ₃ S ₂ H ₃	342.41	≈ 2.28	≈ 150
C ₄ A \bar{S} H ₁₂	622.51	1.95	319.24
C ₄ AH ₁₃	560.47	2.06	272.07
C ₃ A.3C \bar{S} .H ₃₂	1255.13	1.78	705.13
C ₆ AFH ₁₂	814.31	2.65	307.87
C ₈ AF \bar{S} ₂ H ₂₄	1302.44	≈ 2.3	≈ 560
C ₈ AFH ₂₆	1178.29	≈ 2.3	≈ 500
C \bar{C}	100.09	2.71	36.93
C	56.08	3.32	16.89
S	60.08	2.20	27.28
A	101.96	4.00	25.49
F	159.69	5.24	30.48
\bar{S}	80.07	-	-

*Values taken from refs. [26,36-38]

In the above equations, free CaO was assumed to be completely converted to CH, whereas the remaining oxides (MgO, Na₂O, K₂O) was assumed not to participate in the reactions.

The *concrete porosity*, ε , defined as the ratio of pore volume to the total volume of concrete, is given by [11]:

$$\varepsilon = \varepsilon_0 - \Delta\varepsilon_h - \Delta\varepsilon_p - \Delta\varepsilon_c \quad (3.2.14)$$

where ε_0 is the *porosity of fresh concrete*, and $\Delta\varepsilon_h$, $\Delta\varepsilon_p$, $\Delta\varepsilon_c$ are the *porosity reductions* due to hydration of portland clinker, pozzolanic activity, and carbonation, respectively. The initial value of porosity ε_0 is given by the expression:

$$\varepsilon_0 = \varepsilon_{\text{air}} + W/d_w \quad (3.2.15)$$

where ε_{air} is the volume fraction of entrapped or entrained air in concrete (m^3/m^3), W the initial water content in concrete (kg/m^3) and d_w the water density ($\approx 1000 \text{ kg}/\text{m}^3$). The reduction terms in Eq. (3.2.14) are due to the fact that the molar volume of the solid products of hydration, pozzolanic and carbonation reactions exceed that of the solid reactants.

For portland clinker concrete the term $\Delta\varepsilon_p$ equals zero. The term $\Delta\varepsilon_h$ is calculated by the following equation:

$$\Delta\varepsilon_h = \{(C_3S)\Delta\bar{V}_{C_3S} + (C_2S)\Delta\bar{V}_{C_2S} + (C_3A)\Delta\bar{V}_{C_3A} + (C_4AF)\Delta\bar{V}_{C_4AF}\} K \quad (3.2.16)$$

where, $\Delta\bar{V}_j$ ($j= C_3S, C_2S, C_3A, C_4AF$) are the differences in molar volumes between solid products and solid reactants in hydration reactions, in m^3/kg . They can be calculated knowing the stoichiometry of the reactions and the molar volumes of the solid reactants and products (given in Table 3.2.1). For example, in the case of C_3S :

$$\begin{aligned} \Delta\bar{V}_{C_3S} &= (3/2 \times 33.08 \times 10^{-6} + 1/2 \times 150 \times 10^{-6} - 71.34 \times 10^{-6}) / (228.30 \times 10^{-3}) \\ &= 0.2334 \times 10^{-3} \text{ m}^3/\text{kg } C_3S \end{aligned}$$

Similarly, $\Delta\bar{V}_{C_2S}=0.2285 \times 10^{-3} \text{ m}^3/\text{kg } C_2S$, $\Delta\bar{V}_{C_3A}=0.5769 \times 10^{-3} \text{ m}^3/\text{kg } C_3A$, and $\Delta\bar{V}_{C_4AF}=0.2321 \times 10^{-3} \text{ m}^3/\text{kg } C_aAF$. By substituting these values and the Eq.(3.2.5)-(3.2.8) in the Eq. (3.2.16), the *final value of the concrete porosity* can be obtained by the expression:

$$\varepsilon = \varepsilon_{\text{air}} + W/d_w - \{0.249(f_{C,K} - 0.7f_{\bar{S},K}) + 0.191f_{S,K} + 1.118f_{A,K} - 0.357f_{F,K}\} (K/1000) \quad (3.2.17)$$

The reduction term due to the *complete concrete carbonation* is given by:

$$\Delta\varepsilon_c = (\text{CH})\Delta\bar{V}_{\text{CH}} + (\text{CSH})\Delta\bar{V}_{\text{CSH}} \quad (3.2.18)$$

where $\Delta\bar{V}_{\text{CH}}$ ($=0.05196 \times 10^{-3} \text{ m}^3/\text{kgCH}$), and $\Delta\bar{V}_{\text{CSH}}$ ($=0.04495 \times 10^{-3} \text{ m}^3/\text{kg CSH}$), the differences in molar volumes between solid products and reactants in carbonation reaction of CH and CSH, respectively. Knowing the CH and CSH contents, the porosity reduction due to carbonation can be determined using Eq. (3.2.18) for all types of concrete.

b. Cement type CEM I with concrete additions: silica fume and/or fly ash

In this case we suppose that we have a type CEM I cement and may have also as concrete's additions: silica fume and/or fly ash (either siliceous or calcareous). When silica fume is added, the weight fraction of S in silica fume, $f_{S,S}$, and its active part, $\gamma_{S,S}$, are relevant to the quantitative calculations. When a siliceous fly ash is added, the weight fractions of S and A in fly ash, $f_{S,F}$ and $f_{A,F}$, and their active part, $\gamma_{S,F}$ and $\gamma_{A,F}$, are relevant to the quantitative calculations. In addition when the fly ash is calcareous, the weight fractions of C and \bar{S} in fly ash, $f_{C,F}$ and $f_{\bar{S},F}$, are also used.

When additions are used in concrete, in addition to portland clinker hydration reactions, the pozzolanic reactions (3.1.9)-(3.1.13) take place. We assume that, the sulphate content, both from cement and additions, is higher than that required for the full hydration of the clinker and the completion of the pozzolanic reactions. Taking into account the stoichiometry of these reactions, after complete evolution of the hydration and pozzolanic action, the following “final” contents are calculated [31-34]:

$$\begin{aligned} \mathbf{CH} &= \{ 1.321 (f_{C,K} - 0.7 f_{S^-,K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} K \\ &\quad - 1.851 \gamma_{S,S} f_{S,S} S \\ &\quad - \{ (1.851 \gamma_{S,F} f_{S,F} + 2.182 \gamma_{A,F} f_{A,F}) - 1.321 (f_{C,F} - 0.7 f_{S^-,F}) \} F \end{aligned} \quad (3.2.19)$$

$$\mathbf{CSH} = 2.85 (f_{S,K} K + \gamma_{S,S} f_{S,S} S + \gamma_{S,F} f_{S,F} F) \quad (3.2.20)$$

$$\mathbf{CA\bar{S}H} = (6.106 f_{A,K} - 3.898 f_{F,K}) K + 6.106 \gamma_{A,F} f_{A,F} F \quad (3.2.21)$$

$$\mathbf{CAFH} = 5.099 f_{F,K} K \quad (3.2.22)$$

$$\begin{aligned} \mathbf{H} &= \{ 0.321 (f_{C,K} - 0.7 f_{S^-,K}) + 1.236 f_{A,K} - 0.113 f_{F,K} \} K \\ &\quad + \{ 0.321 (f_{C,F} - 0.7 f_{S^-,F}) + 1.236 \gamma_{A,F} f_{A,F} \} F \end{aligned} \quad (3.2.23)$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{\min} > H$. Similarly, the minimum water to cement ratio $(W/C)_{\min}$ is defined as H/C .

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.19) must be positive (i.e., $CH \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of silica fume and fly ash. Writing again Eq. (3.2.19) as:

$$\mathbf{CH} = q_K K - q_S S - q_F F \quad (3.2.19a)$$

where:

$$q_K = \{ 1.321 (f_{C,K} - 0.7 f_{S^-,K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} \quad (3.2.19b)$$

$$q_S = \{ 1.851 \gamma_{S,S} f_{S,S} \} \quad (3.2.19c)$$

$$q_F = \{ (1.851 \gamma_{S,F} f_{S,F} + 2.182 \gamma_{A,F} f_{A,F}) - 1.321 (f_{C,F} - 0.7 f_{S^-,F}) \} \quad (3.2.19d)$$

we distinguish the below cases; determining simultaneously the *maximum part of silica fume that may participate in the pozzolanic reactions (defined as S_{ACT})* and the *corresponding part for fly ash (defined as F_{ACT})*:

a. If only silica fume is added ($F=0$ and $S \neq 0$):

$$S \leq (q_K / q_S) K, \quad \text{then: } S_{ACT} = S \quad (3.2.24a)$$

$$S > (q_K / q_S) K, \quad \text{then: } S_{ACT} = (q_K / q_S) K \quad (3.2.24b)$$

In the latter case, the $CH=0$, and the rest of silica fume ($S-S_{ACT}$) is inert.

b. If only fly ash is added ($S=0$ and $F \neq 0$):

$$F \leq (q_K / q_F) K, \quad \text{then: } F_{ACT} = F \quad (3.2.25a)$$

$$F > (q_K / q_F) K, \quad \text{then: } F_{ACT} = (q_K / q_F) K \quad (3.2.25a)$$

In the latter case, the $CH=0$, and the rest of fly ash ($F-F_{ACT}$) is inert.

c. If both silica fume and fly ash are added ($S \neq 0$ and $F \neq 0$):

$$q_S S + q_F F \leq q_K K, \quad \text{then: } S_{ACT} = S \text{ and } F_{ACT} = F \quad (3.2.26a)$$

$$q_S S + q_F F > q_K K \quad \text{then: } S_{ACT} = S \text{ and } F_{ACT} = [(q_K / q_F) K - (q_S / q_F) S] \quad (3.2.26b)$$

In the latter case, the $CH=0$, and if $S \leq (q_K / q_S) K$ (as usually valid – otherwise go to the case *a.*, with all fly ash inert), then the whole quantity of silica fume will react preferably with the produced CH from clinker hydration, and afterwards, part of fly ash will react with any remaining CH . Thus in the latter case only the $F_{ACT} = [(q_K / q_F) K - (q_S / q_F) S]$ of fly ash is active and the rest of fly ash ($F-F_{ACT}$) is inert.

Obviously, the active contents must be inserted in the Eq. (3.2.19)-(3.2.23), as well in the following determining porosity. In the case when active CaO is added, i.e., as lime putty, this is added to the CH content increasing thus the active parts of silica fume and/or fly ash [39-41].

The porosity reduction, because of the pozzolanic reaction ($\Delta\varepsilon_p$) of silica fume is negligible [32], and only the pozzolanic reaction of fly ash decreases porosity. If the gypsum content is higher than the maximum required, the term $\Delta\varepsilon_p$ is calculated as:

$$\Delta\varepsilon_p = (\gamma_A f_{A,F} F) \Delta \bar{V}_{A,\bar{S}} + (f_{C,F} - 0.7f_{\bar{S},F}) F \Delta \bar{V}_C \quad (3.2.27)$$

where $\Delta \bar{V}_{A,\bar{S}}$ and $\Delta \bar{V}_C$ are the molar volume differences for the reactions (3.1.10) and (3.1.13) respectively (equal to $1.18 \times 10^{-3} \text{ m}^3/\text{kg}$ and $0.289 \times 10^{-3} \text{ m}^3/\text{kg}$ respectively). By substituting the $\Delta\varepsilon_h$ and $\Delta\varepsilon_p$ terms in Eq. (3.2.14), the *final* value of the porosity, ε , of a non-

carbonated concrete (cement CEM I and using additions silica fume and/or fly ash), and ε_C of a totally carbonated concrete, are given by:

$$\varepsilon = \varepsilon_{\text{air}} + W/d_w - \{ 0.249 (f_{C,K} - 0.7 f_{\bar{S},K}) + 0.191 f_{S,K} + 1.118 f_{A,K} - 0.357 f_{F,K} \} (K/1000) - \{ 0.289 (f_{C,F} - 0.7 f_{\bar{S},F}) + 1.18 \gamma_{A,F} f_{A,F} \} (F/1000) \quad (3.2.28)$$

$$\varepsilon_C = \varepsilon - \{ (CH) 0.05196 \times 10^{-3} + (CSH) 0.04495 \times 10^{-3} \} \quad (3.2.29)$$

Typical values of $f_{i,K}$ and $f_{i,P}$, i.e., *the weight fractions of the constituent i* ($i=C, S, A, F, \bar{S}$) in the portland clinker and various SCM, respectively, are presented in Table 3.2.2. The oxide activity ratios also for each SCM, $\gamma_{i,P}$, is included (a mean value, both for silica and alumina).

Table 3.2.2 Typical oxide analysis (%) and activity ratios, γ (%), of portland clinker, silica fume, siliceous and calcareous fly ashes, and various SCM used in EN 197 [data from 31-34, 14-20].

	Cementitious/pozzolanic materials	S	A	F	C	\bar{S}	γ
1	Portland clinker	23	6	3	65	0.5	-
2	Blast furnace slag	36	9	1	40	0.5	90
3	Silica fume	91	1	1.5	0.7	0.4	96
4	Pozzolana (natural)	58	15	5	6	1	50
5	Pozzolana (natural, calcined)*	53	42	1	0.1	0	80
6	Siliceous fly ash	53	20	9	4	0.6	82
7	Calcareous fly ash	39	16	6	24	4.3	71
8	Burnt shale	38	10	6	35	5	90
9	Limestone	2	1	0.2	2	0.1	50
10	Various SCM for CEM II	50	16	7	12	1.5	65
11	Various SCM for CEM IV	50	20	7	10	1	65
12	Various SCM for CEM V	50	20	7	10	1	65

* Metakaolin

3.2.2 Cement types CEM II, CEM III, CEM IV

In this general case, we suppose that we have any of types CEM II, CEM III, or CEM IV of cement. No other extra SCM is added as a separate concrete addition. The cement's SCM content in concrete is denoted as P (kg/m^3 of concrete) and is given by Eq. (3.2.2). When SCM exists in cement, in addition to portland clinker hydration reactions, the pozzolanic reactions (3.1.9)-(3.1.13) take place. We assume that, the sulphate content, both from cement and SCM, is higher than that required for the full hydration of the clinker and the completion of the pozzolanic reactions. Taking into account the previous analysis, the following "final" contents and porosities are calculated:

$$\begin{aligned} \mathbf{CH} &= \{ 1.321 (f_{C,K} - 0.7 f_{\bar{S},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} K \\ &\quad - \{ (1.851 \gamma_{S,P} f_{S,P} + 2.182 \gamma_{A,P} f_{A,P}) - 1.321 (f_{C,P} - 0.7 f_{\bar{S},P}) \} P \end{aligned} \quad (3.2.30)$$

$$\mathbf{CSH} = 2.85 (f_{S,K} K + \gamma_{S,P} f_{S,P} P) \quad (3.2.31)$$

$$\mathbf{CA\bar{S}H} = (6.106 f_{A,K} - 3.898 f_{F,K}) K + 6.106 \gamma_{A,P} f_{A,P} P \quad (3.2.32)$$

$$\mathbf{CAFH} = 5.099 f_{F,K} K \quad (3.2.33)$$

$$\begin{aligned} \mathbf{H} &= \{ 0.321 (f_{C,K} - 0.7 f_{\bar{S},K}) + 1.236 f_{A,K} - 0.113 f_{F,K} \} K \\ &\quad + \{ 0.321 (f_{C,P} - 0.7 f_{\bar{S},P}) + 1.236 \gamma_{A,P} f_{A,P} \} P \end{aligned} \quad (3.2.34)$$

$$\begin{aligned} \boldsymbol{\varepsilon} &= \varepsilon_{\text{air}} + W/d_w \\ &\quad - \{ 0.249 (f_{C,K} - 0.7 f_{\bar{S},K}) + 0.191 f_{S,K} + 1.118 f_{A,K} - 0.357 f_{F,K} \} (K/1000) \\ &\quad - \{ 0.289 (f_{C,P} - 0.7 f_{\bar{S},P}) + 1.18 \gamma_{A,P} f_{A,P} \} (P/1000) \end{aligned} \quad (3.2.35)$$

$$\boldsymbol{\varepsilon}_C = \varepsilon - \{ (\mathbf{CH}) 0.05196 \times 10^{-3} + (\mathbf{CSH}) 0.04495 \times 10^{-3} \} \quad (3.2.36)$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{\min} > H$.

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.30) must be positive ($\mathbf{CH} \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of SCM. Writing again Eq. (3.2.30) as follows:

$$\mathbf{CH} = q_K K - q_P P \quad (3.2.30a)$$

where:

$$q_K = \{ 1.321 (f_{C,K} - 0.7 f_{\bar{s},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} \quad (3.2.30b)$$

$$q_P = \{ (1.851 \gamma_{S,P} f_{S,P} + 2.182 \gamma_{A,P} f_{A,P}) - 1.321 (f_{C,P} - 0.7 f_{\bar{s},P}) \} \quad (3.2.30c)$$

the following condition has always to be considered; determining the *maximum part of SCM that may participate in the pozzolanic reactions (defined as P_{ACT})*:

$$P \leq (q_K / q_P) K, \quad \text{then: } P_{ACT} = P \quad (3.2.37a)$$

$$P > (q_K / q_P) K, \quad \text{then: } P_{ACT} = (q_K / q_P) K \quad (3.2.37b)$$

In the latter case, the $CH=0$, and the rest of SCM: $(P-P_{ACT})$ is inert.

Obviously, the active contents must be inserted in the Eq. (3.2.30)-(3.2.36).

3.2.3 Cement type CEM V

In this case, we suppose that we have a type CEM V cement. No other extra SCM is added to the concrete mixture. This composite cement contains, apart the clinker, certain amounts of both slag and other pozzolanic materials. The p_{SCM} (%) percentage of the total SCM in the cement (minus calcium sulphate) is separated in p_{SL} (%), referring to slag percentage in cement, and $p_{PO} = (p_{SCM} - p_{SL})$, referring to the other pozzolanic materials. The cement's slag content in concrete, denoted by SL (kg/m^3 of concrete), and the cement's pozzolan content (except slag) in concrete, denoted by P (kg/m^3 of concrete), are given by:

$$SL = (p_{SL}/100) C (100-p_{CS})/100 \quad (3.2.38)$$

$$P = [(p_{SCM} - p_{SL})/100] C (100-p_{CS})/100 \quad (3.2.39)$$

Taking into account the previous analysis, the following "*final*" contents and porosities are then calculated:

$$CH = \{ 1.321 (f_{C,K} - 0.7 f_{\bar{s},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} K$$

$$\begin{aligned}
 & - \{ (1.851 \gamma_{S,SL} f_{S,SL} + 2.182 \gamma_{A,SL} f_{A,SL}) - 1.321 (f_{C,SL} - 0.7 f_{\bar{S},SL}) \} SL \\
 & - \{ (1.851 \gamma_{S,P} f_{S,P} + 2.182 \gamma_{A,P} f_{A,P}) - 1.321 (f_{C,P} - 0.7 f_{\bar{S},P}) \} P \quad (3.2.40)
 \end{aligned}$$

$$\mathbf{CSH} = 2.85 (f_{S,K} K + \gamma_{S,SL} f_{S,SL} SL + \gamma_{S,P} f_{S,P} P) \quad (3.2.41)$$

$$\begin{aligned}
 \mathbf{H} & = \{ 0.321 (f_{C,K} - 0.7 f_{\bar{S},K}) + 1.236 f_{A,K} - 0.113 f_{F,K} \} K \\
 & + \{ 0.321 (f_{C,SL} - 0.7 f_{\bar{S},SL}) + 1.236 \gamma_{A,SL} f_{A,SL} \} SL \\
 & + \{ 0.321 (f_{C,P} - 0.7 f_{\bar{S},P}) + 1.236 \gamma_{A,P} f_{A,P} \} P \quad (3.2.42)
 \end{aligned}$$

$$\begin{aligned}
 \boldsymbol{\varepsilon} & = \varepsilon_{\text{air}} + W/d_w \\
 & - \{ 0.249 (f_{C,K} - 0.7 f_{\bar{S},K}) + 0.191 f_{S,K} + 1.118 f_{A,K} - 0.357 f_{F,K} \} (K/1000) \\
 & - \{ 0.289 (f_{C,SL} - 0.7 f_{\bar{S},SL}) + 1.18 \gamma_{A,SL} f_{A,SL} \} (SL/1000) \\
 & - \{ 0.289 (f_{C,P} - 0.7 f_{\bar{S},P}) + 1.18 \gamma_{A,P} f_{A,P} \} (P/1000) \quad (3.2.43)
 \end{aligned}$$

$$\boldsymbol{\varepsilon}_C = \boldsymbol{\varepsilon} - \{ (\text{CH}) 0.05196 \times 10^{-3} + (\text{CSH}) 0.04495 \times 10^{-3} \} \quad (3.2.44)$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{\min} > H$.

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.40) must be positive ($\text{CH} \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of slag and pozzolans. Rewriting Eq. (3.2.40) as follows:

$$\text{CH} = q_K K - q_{SL} SL - q_P P \quad (3.2.40a)$$

where:

$$q_K = \{ 1.321 (f_{C,K} - 0.7 f_{\bar{S},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} \quad (3.2.40b)$$

$$q_{SL} = \{ (1.851 \gamma_{S,SL} f_{S,SL} + 2.182 \gamma_{A,SL} f_{A,SL}) - 1.321 (f_{C,SL} - 0.7 f_{\bar{S},SL}) \} \quad (3.2.40c)$$

$$q_P = \{ (1.851 \gamma_{S,P} f_{S,P} + 2.182 \gamma_{A,P} f_{A,P}) - 1.321 (f_{C,P} - 0.7 f_{\bar{S},P}) \} \quad (3.2.40d)$$

the following condition has always to be considered; determining the *maximum parts of slag and pozzolan that may participate in the pozzolanic reactions (defined respectively as SL_{ACT} and P_{ACT})*:

$$q_{SL} SL + q_P P \leq q_K K, \text{ then: } SL_{ACT} = SL \text{ and } P_{ACT} = P \quad (3.2.45a)$$

$$q_{SL} SL + q_P P > q_K K \quad (3.2.45b)$$

In the latter case, the $CH=0$, and assuming that both slag and pozzolans react at the same rate with the produced CH , we calculate this similar degree of reaction, r , as follows:

$$r = (q_K K) / (q_{SL} SL + q_P P) \quad (3.2.46)$$

Then, only the $(r SL)$ of slag is active (SL_{ACT}) and the rest $[(1-r) SL]$ is inert. Similarly, only the $(r P)$ of the pozzolanic materials is active (P_{ACT}) and the rest $[(1-r) P]$ is inert.

3.3 Estimation of reaction kinetics

Expressions for the rates, $r_{h,i}$ (mol/m³.s), of the *hydration reaction* of the portland clinker phases ($i = C_3S, C_2S, C_3A, C_4AF$) have been presented in a previous publication [11]. They were obtained from measurements [24,27] of the fraction $F_{h,i}(t)$ of compound i , which has been hydrated at time t (s) after mixing (*degree of hydration*), and have the form:

$$r_{h,i} \equiv -dC_i/dt = k_{h,i} C_i^{n_i} / C_{i,0}^{n_i-1} \quad (3.3.1)$$

$$F_{h,i} \equiv 1 - C_i / C_{i,0} = 1 - [1 - k_{h,i} t(1-n_i)]^{1/(1-n_i)} \quad (3.3.2)$$

in which C_i and $C_{i,0}$ are the current and the initial (at $t=0$) molar concentrations of compound i , respectively (mol/m³), $k_{h,i}$ and n_i kinetic parameters for the compound i depending on fineness, curing conditions and temperature. Fitted values of the exponents n_i and the coefficients $k_{h,i}$ (for curing temperature of 20 °C) are listed in Table 3.3.1. For another curing temperature, θ (°C), the following relationship may be used [1]:

$$k_{h,i} = k_{h,i}(20^\circ\text{C}) \exp [(E/R) (1/293 - 1/(273+\theta))] \quad (3.3.3a)$$

$$E = 33500 + 1470(20-\theta) \text{ for } \theta < 20^\circ\text{C}, \text{ and} \quad (3.3.3b)$$

$$E = 33500 \text{ for } \theta \geq 20^\circ\text{C} \quad (3.3.3c)$$

Table 3.3.1 Hydration parameters for major clinker components*.

	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Exponent n _i	2.65	3.10	2.41	3.81
Coefficient k _{h,i} × 10 ³ , kg/gmol	1.17	0.16	2.46	1.00

*for CEM I 42.5N, 20 °C

where E is the mean activation energy for the hydration reactions (J/gmol) and R the gas universal constant (8.314 J/gmol.K)

Similar rate expressions can describe the *pozzolanic reactions*, Eq. (3.1.9)-(3.1.13). In this case, the pozzolanic activity is revealed after a certain period of time, denoted as t*, (“incubation period” of pozzolanic activity). This period is approximately 1 day for silica fume, 2 weeks for low-calcium fly ash and 3 days for high-calcium fly ash or blast furnace slag [14]. Thus, the reaction rate, r_{p,j}, of an active oxide j of the pozzolan (j=S,A,C) can be described as follows:

$$r_{p,j} = 0, \quad 0 \leq t \leq t^* \quad (3.3.4)$$

$$r_{p,j} \equiv -dC_j/dt = k_{p,j} C_{j,0} (1-F_{p,j})^{n_j} = k_{p,j} C_j^{n_j} / C_{j,0}^{n_j-1}, \quad t^* \leq t \quad (3.3.5)$$

$$F_{p,j} \equiv 1 - C_j / C_{j,0} = 1 - [1 - k_{p,j} t(1-n_j)]^{1/(1-n_j)} \quad (3.3.6)$$

By fitting these expressions in experimental results of fraction F_{p,j} of reacted oxide j as a function of time, the parameter values can be obtained. Usually, only CH-content and compressive strength results are available for the estimation of the degree of pozzolanic reaction. However, as was observed in H-content results [31], the presence of SCM in concrete *alters* the hydration rates of the clinker compounds. Therefore, the CH-content or the strength differences at an intermediate time cannot be attributed exclusively to pozzolanic reactions. For example, the C₃A and C₄AF hydration is significantly retarded in the presence of pozzolans. A complete kinetic analysis should include the hydration rate alterations of the portland clinker individual compounds. With the present results, such analysis is not possible.

Moreover, in such a case the final picture would be very complicated. Thus, the *development degree of the main concrete characteristics (CH-content, porosity, strength)* can be estimated better using the experimental results given in this or similar works, leaving the pure fundamental approach for a future work.