The Work by Powers and Brownyard Revisited: Part 3

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Abstract

In this paper the individual reactions of the four clinker phases: alite, belite, aluminate and ferrite, and of the calcium sulphate phases, as derived previously [1, 2], are applied to predict the composition of cement paste. These reactions for Portland cement were formulated and based on the water retentions and compressed water data provided by Powers and Brownyard [3]. Using these hydration reactions, the types and quantities of the hydration products formed are quantified, in absolute and relative terms. This results in analytical expressions that give the composition of the hydration product (at 80% and 100% relative humidity), which is one of the four compartments in the paste model of [3], the three other ones being capillary water, unreacted cement, and shrinkage. The model is applied to a typical CEM I, and it is seen that full hydration is possible at 80% RH with a w_0/c_0 as low as 0.27.

1. Introduction

In a pioneering work, Powers and Brownyard [3] were the first to systematically investigate the reaction of cement and water and the formation of cement paste. In the late 1940s they presented a thorough model of the cement paste, in which unreacted water and cement, the hydration product, and (gel and capillary) porosity were considered. Via extensive and carefully executed experiments major paste properties were determined such as the amount of retained water and the chemical shrinkage associated with the hydration reaction. These properties were furthermore related to the content of the four most important clinker phases, viz. alite, belite, aluminate and ferrite, in the cement. Locher [4], Hansen [5], Taylor [6], Neville [7] and Brouwers [1, 2] summarize the most important features of their work. In [1, 2] their water retention data was used to specify the hydration reactions of the 5 most important cement phases. Here, it will be demonstrated that this result enables the quantification of mass and volume distribution of the various hydration products as a function of the clinker composition and degree of hydration. This can be considered as a refinement of the volume model of the cement paste as presented by Powers and Brownyard [3], who

distinguished unreacted water, unreacted cement, chemical shrinkage and the hydration product, without specifying the latter.

2. Cement paste model

Based on the work of Powers and Brownyard [3], Brouwers [1, 2] put forward the following volume relations of hydration product, unhydrated cement, unreacted water and chemical shrinkage (Figure 1):

$$\varphi_{hp} = \frac{V_{hp}}{V_t} = \frac{\left[\dfrac{V_{hp}}{v_w c_0}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{\left[\dfrac{v_c c}{v_w c_0} + \dfrac{w_d v_d}{v_w c_0}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{m\left[\dfrac{v_c}{v_w} + \dfrac{w_d v_d}{v_w c}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad ; \quad (1)$$

$$\varphi_c = \frac{V_c}{V_t} = \frac{(1-m)\left[\dfrac{v_c}{v_w}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad ; \quad\quad (2)$$

$$\varphi_w = \frac{V_w}{V_t} = \frac{\dfrac{V_w}{v_w c_0}}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{\dfrac{w_0 - w_d}{c_0}}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{\dfrac{w_0}{c_0} - m\left[\dfrac{w_d}{c}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad\quad (3)$$

and

$$\varphi_s = \frac{V_s}{V_t} = \frac{\dfrac{V_s}{v_w c_0}}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{\dfrac{w_d}{c_0} - \dfrac{w_d v_d}{v_w c_0}}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{m\left[\dfrac{w_d}{c} - \dfrac{w_d v_d}{v_w c}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad , \quad (4)$$

respectively. It readily follows that $\varphi_c + \varphi_{hp} + \varphi_w + \varphi_s = 1$, so the total paste volume is completely comprised by these four fractions indeed. As ratio of specific volumes of cement and free water (v_c/v_w), 0.32 can be taken, w_0/c_0 represents the water cement ratio, and V_w and V_c the initial volumes of mixing water and cement, respectively ($V_w + V_c = V_t$). Eqs. (1)-(4) also contain the maturity m, which is a function of time, and depends among others on the cement composition, its fineness, the temperature and the w_0/c_0.
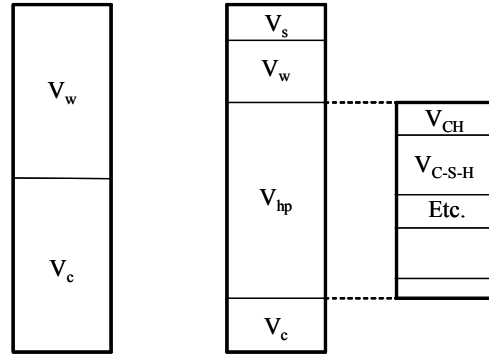
a) Initial situation   b) Upon hydration

Figure 1 Breakdown of cement paste model into 4 phases, and of the hydration product into the individual hydration products ($m = 0$ and $m > 0$).

The water retention and retained water volume, chemically and physically, depend on the composition of the cement and read [8, 9]

$$w_d/c = 0.355 \ x_{C_3S} + 0.366 \ x_{C_2S} + 1.401 \ x_{C_3A} +$$

$$0.482 \ x_{C_4AF} + (0.355 \ \alpha - 0.091) \ x_{C\bar{S}} , \qquad (5)$$

$$\frac{w_d v_d}{v_w c} = 0.281 \ x_{C_3S} + 0.306 \ x_{C_2S} + 1.103 \ x_{C_3A} +$$

$$0.396 \ x_{C_4AF} + (0.330 \ \alpha - 0.095) \ x_{C\bar{S}} , \qquad (6)$$

respectively. In eqs. (1)-(6), c stands for the reacted cement (= $m \ c_0$). In eqs. (5) and (6) the degree of carbonation α appears, which governs the fraction mono-sulphate that is carbonated ($0 \leq \alpha \leq 1$) [2].

3. Cement paste model with individual reactions

The above equations are based on the water retention data by Powers and Brownyard [3] and the reaction scheme derived there from by Brouwers [1, 2], which is summarized in Table 1.
Next, by employing the specific density of each substance involved [2], the mass reaction scheme is expressed in volume, the result being included in Table 3. In Tables 2 and 3 the uncombined oxides appear, comprising the remaining oxides (x_{RO} [1]) which are the oxides *not* included in Bogue's formulas (C, S, A, F and $\bar{S}$) and a 0.116α term that accounts for the mass

of $C\bar{C}$ per mass of reacted cement that enters the hydration product (and which is not provided by the major oxides), viz. $x_{C\bar{C}} = 0.116\,\alpha\,x_{C\bar{S}}$ [2, 8, 9].

$$n_{C_6AFS_2H_{18}} = n_{C_4AF}$$

$$n_{C_6A\bar{S}_3H_{36}} = \tfrac{1}{57}(10+9\alpha)n_{C\bar{S}}$$

$$n_{C_4A\bar{S}H_{14}} = \tfrac{9}{19}(1-\alpha)n_{C\bar{S}}$$

$$n_{C_4A\bar{C}_{0.5}H_{12}} = \tfrac{6}{19}\alpha n_{C\bar{S}}$$

$$n_{C_4AH_{22}} = n_{C_3A} - \tfrac{37}{57}n_{C\bar{S}}$$

$$n_{C_{1.7}SH_{3.2}} = n_{C_3S} + n_{C_2S} - 2n_{C_4AF}$$

$$n_{CH} = 1.3n_{C_3S} + 0.3n_{C_2S} - n_{C_3A} + 1.4n_{C_4AF} + n_{C\bar{S}}(\tfrac{37}{57} - \tfrac{3}{19}\alpha)$$

Table 1 Reaction scheme (in moles)

By employing the molar mass each substance involved [2], the molar reaction scheme is expressed in mass, see Table 2.

$$m_{C_6AFS_2H_{18}}/c = 2.146\ x_{C_4AF}$$

$$m_{C_6A\bar{S}_3H_{36}}/c = (1.710 + 1.540\ \alpha)\ x_{C\bar{S}}$$

$$m_{C_4A\bar{S}H_{14}}/c = 2.292\ (1 - \alpha)\ x_{C\bar{S}}$$

$$m_{C_4A\bar{C}_{0.5}H_{12}}/c = 1.309\ \alpha\ x_{C\bar{S}}$$

$$m_{C_4AH_{22}}/c = 2.675\ x_{C_3A} - 3.446\ x_{C\bar{S}}$$

$$m_{C_{1.7}SH_{3.2}}/c = 0.933\ x_{C_3S} + 1.237\ x_{C_2S} - 0.877\ x_{C_4AF}$$

$$m_{CH}/c = 0.422\ x_{C_3S} + 0.129\ x_{C_2S} - 0.274\ x_{C_3A} + 0.213\ x_{C_4AF} + (0.353 - 0.086\ \alpha)\ x_{C\bar{S}}$$

$$m_{UO}/c = x_{UO} = 1 - x_{C_3S} - x_{C_2S} - x_{C_3A} - x_{C_4AF} - (1 + 0.116\ \alpha)\ x_{C\bar{S}}$$

Table 2 Reaction scheme (in mass)

Note that the total of all masses listed in Table 2 equals:

$$m_{hp} = c + w_d \qquad , \tag{7}$$

see eq. (5), where m_{hp} is the mass of the hydration product (reacted cement + retained water). The total of all volumes listed in Table 3 equals:

$$V_{hp}/v_w c = 0.32 + 0.281\ x_{C_3S} + 0.306\ x_{C_2S} + 1.103\ x_{C_3A} + 0.396\ x_{C_4AF} + (0.330\ \alpha - 0.095)\ x_{C\bar{S}}, \tag{8}$$

see eqs. (1) and (6), and using $v_c/v_w = 0.32$ [8, 9], where V_{hp} is the volume of the hydration product (Figure 1).

$$V_{C_6AFS_2H_{18}}/v_wc = 0.958 \ x_{C_4AF}$$

$$V_{C_6A\bar{S}_3H_{36}}/v_wc = (0.994 + 0.895 \ \alpha) \ x_{C\bar{S}}$$

$$V_{C_4A\bar{S}H_{14}}/v_wc = 1.144 \ (1 - \alpha) \ x_{C\bar{S}}$$

$$V_{C_4A\bar{C}_{0.5}H_{12}}/v_wc = 0.660 \ \alpha \ x_{C\bar{S}}$$

$$V_{C_4AH_{22}}/v_wc = 1.552 \ x_{C_3A} - 2.000 \ x_{C\bar{S}}$$

$$V_{C_{1.7}SH_{3.2}}/v_wc = 0.414 \ x_{C_3S} + 0.549 \ x_{C_2S} - 0.389 \ x_{C_4AF}$$

$$V_{CH}/v_wc = 0.188 \ x_{C_3S} + 0.058 \ x_{C_2S} - 0.122 \ x_{C_3A} +$$
$$0.095 \ x_{C_4AF} + (0.158 - 0.038 \ \alpha) \ x_{C\bar{S}}$$

$$V_{UO}/v_wc = 0.32 - 0.321 \ x_{C_3S} - 0.301 \ x_{C_2S} - 0.327 \ x_{C_3A}$$
$$- 0.268 \ x_{C_4AF} - (0.391 + 0.043 \ \alpha) \ x_{C\bar{S}}$$

Table 3 Reaction scheme (in volume)

Note that the volumes given in Table 3 can also be used to assess the volume fraction of each hydration product in the entire paste, the total of them constituting the hydration product volume fraction (eq. (1)). For example, the volume (fraction) of the C-S-H in the paste reads read

$$\varphi_{C\text{-}S\text{-}H} = \frac{V_{C\text{-}S\text{-}H}}{V_t} = \frac{\left[\dfrac{V_{C\text{-}S\text{-}H}}{v_wc_0}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} = \frac{m\left[\dfrac{V_{C\text{-}S\text{-}H}}{v_wc}\right]}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}}$$

$$= \frac{m(0.414\,x_{C_3S} + 0.549\,x_{C_2S} - 0.389\,x_{C_4AF})}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad , \qquad (9)$$

and whereby $V_{C\text{-}S\text{-}H}/v_wc$ is taken from Table 3. In Figure 1 this feature of the new hydration model is depicted.

4. Incongruent hydration

So far, all five cement phases have been assumed to react congruently. Here, it will be explained how the paste model can handle unequal maturities of all considered cement phases, denoted as m_{C_3S}, m_{C_2S} etc,

each a function of time and each of them ranging from zero to unity. By definition, the overall cement maturity follows from

$$m = \frac{m_{C_3S}\, x_{C_3S} + m_{C_2S}\, x_{C_2S} + m_{C_3A}\, x_{C_3A} + m_{C_4AF}\, x_{C_4AF} + m_{C\bar{S}}\, x_{C\bar{S}}}{x_{C_3S} + x_{C_2S} + x_{C_3A} + x_{C_4AF} + x_{C\bar{S}}} \quad . \tag{10}$$

$$\frac{m_{C_3S}\, x_{C_3S} + m_{C_2S}\, x_{C_2S} + m_{C_3A}\, x_{C_3A} + m_{C_4AF}\, x_{C_4AF} + m_{C\bar{S}}\, x_{C\bar{S}}}{1 - x_{RO}} \quad ,$$

whereby x_{RO} stands for the remaining oxides, i.e. all oxides with except of the five major cement oxides. When the maturities of all five major phases are unity, the overall cement maturity m also should reach unity, which is a consequence of the introduced denominator, which is needed for this purpose. When all five cement phases are fully hydrated, the entire cement is namely taken to be as fully reacted. That is to say, the remaining oxides are present in the hydration product, and are not considered as unreacted cement (Figure 1).

As example, the formation of C-S-H is reconsidered in case the individual phase maturities vary. The formula for the formation of C-S-H, listed in Table 2, is actually based on

$$m_{C_{1.7}SH_{3.2}} / c_0 = (0.933\ x_{C_3S} + 1.237\ x_{C_2S} - 0.877\ x_{C_4AF})\, m \quad . \tag{11}$$

In eq. (11), $0.933\, x_{C_3S}\, m c_0$ stand s for the mass of C-S-H formed by the reacted part of the C_3S mass that is present in the cement, which is not involved in the formation of hydrogarnet, and *mutates mutandis* for C_2S. For non-identical maturities, the non-evaporable water is therefore adequately described by:

$$m_{C_{1.7}SH_{3.2}} / c_0 = 0.933\ m_{C_3S}\, x_{C_3S} + 1.237\ m_{C_2S}\, x_{C_2S} - 0.877\ m_{C_4AF}\, x_{C_4AF} \quad . \tag{12}$$

Now it can be seen that eq. (11) is a special case of eq. (12), namely when $m(t) = m_{C_3S}(t) = m_{C_2S}(t) = m_{C_3A}(t) = m_{C_4AF}(t) = m_{C\bar{S}}(t)$. To apply incongruent maturity development in the paste model, instead of eq. (9), now the C-S-H volume and volume fraction reads

$$\varphi_{C\text{-}S\text{-}H} = \frac{0.414\, m_{C_3S}\, x_{C_3S} + 0.549\, m_{C_2S}\, x_{C_2S} - 0.389\, m_{C_4AF}\, x_{C_4AF}}{\dfrac{v_c}{v_w} + \dfrac{w_0}{c_0}} \quad . \tag{13}$$

So, the quantities of the different hydration products and their volume fraction in the cement paste can be simulated when the maturities of each individual clinker phase is specified (in time). For this purpose, the

expressions of Tables 2 and 3 can be used similarly for the other hydration products as here illustrated by C-S-H.

Note that using this individual reaction model, the total is again eqs. (5) and (8), with c replaced by c_0 in the denominator, and x_{C_3S}, x_{C_2S} etc. by $m_{C_3S} x_{C_3S}$, $m_{C_2S} x_{C_2S}$ etc., respectively. Applied in this way, eqs. (1)-(4) will again yield the paste composition, whereby the hydration product is formed by all individual hydration products, the total of all volume fractions being unity (Figure 1). Similarly, the carbonation process and degree of carbonation is a function of time, $\alpha(t)$, affecting the mass and volume fractions of ettringite, mono-sulphate and hemi-/mono-carbonate.

5 Relative humidity of 80%

The models and equations derived thus far are based on saturated paste, i.e. 100 % relative humidity. In practical application, e.g. in concrete, the bulk of the cement paste is isolated and can effectively be considered as sealed. When the initial amount of water is not sufficient to hydrate all cement to saturated hydration products, so when $w_0/c_0 < w_d/c$ (eq. (14)), during hydration a point can be reached where all capillary water is used. As long as capillary water is present the reactions proceed similar as in the saturated system as given in Tables 2 and 3, and saturated hydration products are formed. But when this water is consumed, the saturated hydration products partly dehydrate with falling relative humidity. Hydration of Portland cement stops at a relative humidity of about 80% [10], this enables the cement hydration to proceed till an equilibrium relative humidity in the entire paste of about 80% is achieved. The water retention, paste composition etc., under this sealed condition is interesting to determine as well. It casts light on the minimum water content required for full hydration of the cement. To this end, first it is necessary to assess the water retention of all hydration products formed at this relative humidity.

It can be expected that the saturated hydrogarnet ($C_6AFS_2H_{18}$), aluminate hydrate (C_4AH_{22}), mono-sulphate ($C_4A\bar{S}H_{14}$) and ettringite ($C_6A\bar{S}_3H_{36}$) lose their most loosely bound water and are readily dehydrated to $C_6AFS_2H_8$, C_4AH_{13}, $C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$, respectively [6]. The portlandite (CH) and hemi-carbonate ($C_4A\bar{C}_{0.5}H_{12}$) retain their water [6]. Brouwers [1] derived that at 80% relative humidity the C-S-H is dehydrated to $C_{1.7}SH_{2.5}$. To assess the quantities (moles) of formed aluminate hydrate, mono-sulphate, hemi-carbonate and ettringite formed, Table 1 can be used. Combining the quantities of the different hydration products and their water retention, results in the following water retention relation at 80% relative humidity:

$$n_{H,d80} = 3.8\ n_{C_3S} + 2.8\ n_{C_2S} + 12\ n_{C_3A} + 4.4\ n_{C_4AF} + (\tfrac{200}{57} + 3\alpha)\ n_{C\bar{S}}. \qquad (14)$$

Using the molar masses of water and clinker phases [1, 2], this equation can be written as

$$w_{d80}/c = 0.300\ x_{C_3S} + 0.293\ x_{C_2S} + 0.800\ x_{C_3A}$$
$$+ 0.163\ x_{C_4AF} + (0.464 + 0.397\alpha)\ x_{C\bar{S}}, \qquad (15)$$

and the reaction scheme of Table 1 be converted in Table 4.

$$m_{C_6AFS_2H_8}/c = 1.775\ x_{C_4AF}$$
$$m_{C_6A\bar{S}3H_{32}}/c = (1.618 + 1.456\ \alpha)\ x_{C\bar{S}}$$
$$m_{C_4A\bar{S}H_{12}}/c = 2.166\ (1 - \alpha)\ x_{C\bar{S}}$$
$$m_{C_4A\bar{C}_{0.5}H_{12}}/c = 1.309\ \alpha\ x_{C\bar{S}}$$
$$m_{C_4AH_{13}}/c = 2.074\ x_{C_3A} - 2.673\ x_{C\bar{S}}$$
$$m_{C_{1.7}SH_{2.5}}/c = 0.878\ x_{C_3S} + 1.164\ x_{C_2S} - 0.825\ x_{C_4AF}$$
$$m_{CH}/c = 0.422\ x_{C_3S} + 0.129\ x_{C_2S} - 0.274\ x_{C_3A} +$$
$$0.213\ x_{C_4AF} + (0.353 - 0.086\ \alpha)\ x_{C\bar{S}}$$
$$m_{UO}/c = x_{UO} = 1 - x_{C_3S} - x_{C_2S} - x_{C_3A} - x_{C_4AF} - (1 + 0.116\ \alpha)\ x_{C\bar{S}}$$

Table 4 Reaction scheme at 80% RH (in mass)

In eq. (14) the factor 4.4 pertaining to C_4AF is introduced to match the factors pertaining to C_3S/C_2S (3.8/2.8).

$$V_{C_6AFS_2H_8}/v_w c = 0.587\ x_{C_4AF}$$
$$V_{C_6A\bar{S}3H_{32}}/v_w c = (0.912 + 0.820\ \alpha)\ x_{C\bar{S}}$$
$$V_{C_4A\bar{S}H_{12}}/v_w c = 1.075\ (1 - \alpha)\ x_{C\bar{S}}$$
$$V_{C_4A\bar{C}_{0.5}H_{12}}/v_w c = 0.660\ \alpha\ x_{C\bar{S}}$$
$$V_{C_4AH_{13}}/v_w c = 1.014\ x_{C_3A} - 1.306\ x_{C\bar{S}}$$
$$V_{C_{1.7}SH_{2.5}}/v_w c = 0.414\ x_{C_3S} + 0.549\ x_{C_2S} - 0.389\ x_{C_4AF}$$
$$V_{CH}/v_w c = 0.188\ x_{C_3S} + 0.058\ x_{C_2S} - 0.122\ x_{C_3A} +$$
$$0.095\ x_{C_4AF} + (0.158 - 0.038\ \alpha)\ x_{C\bar{S}}$$
$$V_{UO}/v_w c = 0.32 - 0.321\ x_{C_3S} - 0.301\ x_{C_2S} - 0.327\ x_{C_3A}$$
$$- 0.268\ x_{C_4AF} - (0.391 + 0.043\ \alpha)\ x_{C\bar{S}}$$

Table 5 Reaction scheme at 80% RH (in volume)

This former factor is required to stoichiometrically permit the formation of $C_6AFS_2H_8$ and 4CH/2CH from $2C_3S/2C_2S$ and C_4AF [2] . The factors pertaining to C_3A and $C\overline{S}$ follow from Table 1, whereby the proper water retention at 80% RH is used, a discussed above. The total mass of all hydration products of Table 4 again complies with eqs. (7) and (15). Using the specific densities of the hydration products, the reaction scheme from Table 4 can be transformed in the volume scheme given in Table 5. The total (scaled) volume of the hydration product follows form Table 5 as

$$V_{hp80} / v_w c = 0.32 + 0.281\ x_{C_3S} + 0.306\ x_{C_2S} +$$
$$0.565\ x_{C_3A} + 0.025\ x_{C_4AF} + (0.448 + 0.324\ \alpha)\ x_{C\overline{S}} . \qquad (16)$$

Similarly as for the saturated paste, the volumes of Table 5 can be used to compute the volume fraction of each individual hydration product by considering eq. (9), or in case of incongruent hydration, eq. (13), which both contain C-S-H as example.
Comparing Tables 3 and 5 it follows that the molar volume of C-S-H is assumed unaffected by the reduction of its gel water content (in contrast to its specific density), and its gel porosity therefore remains 34% [8, 9].

6. Application to CEM I

Here, the paste model is applied to a typical CEM I for which is taken x_{C_3S} = 0.61, x_{C_2S} = 0.15, x_{C_3A} = 0.06, x_{C_4AF} = 0.10 and $x_{C\overline{S}}$ = 0.04. First, the paste in saturated state is described, in the second part of this Section the cement paste at 80% relative humidity (RH) is specified.

6.1 Saturated state

Substituting this composition into eqs. (5) and (6) yields:

$$w_d / c = 0.400 + 0.014\alpha; \quad \frac{w_d v_d}{v_w c} = 0.319 + 0.013\alpha \quad . \qquad (17)$$

It thus follows that w_d/c = 0.400 (no carbonation: α = 0) and w_d/c = 0.414 (full carbonation: α = 1). This value, expressing the amount of water required for full hydration at saturate state, is lower than the value, 0.44, attributed to Powers and Brownyard [6].
Substituting eq. (17), and application of v_c/v_w = 0.32, in eqs. (1)-(4) yield the following volume fractions

$$\varphi_{hp} = \frac{(0.639 + 0.013\,\alpha)m}{0.320 + w_0/c_0} \quad ; \tag{18}$$

$$\varphi_c = \frac{0.320\,(1 - m)}{0.320 + w_0/c_0} \quad ; \tag{19}$$

$$\varphi_w = \frac{w_0/c_0 - (0.400 + 0.014\,\alpha)\,m}{0.320 + w_0/c_0} \quad ; \tag{20}$$

$$\varphi_s = \frac{(0.081 + 0.001\,\alpha)\,m}{0.320 + w_0/c_0} \quad ; \tag{21}$$

respectively. The total capillary porosity now follows as

$$\varphi_{cp} = \varphi_w + \varphi_s = \frac{w_0/c_0 - (0.319 + 0.013\,\alpha)\,m}{0.320 + w_0/c_0} \quad . \tag{22}$$

If water can imbibe, $w_0/c_0 > 0.32$ is sufficient for full hydration. It is theoretically possible for $w_0/c_0 = 0.32$ and full hydration to obtain hydrated paste as the only phase present in the microstructure. If no water can enter the paste, the minimum w_0/c_0 for complete hydration is $0.400 + 0.014\alpha$, see eq. (17), and then voids will be created in the paste by chemical shrinkage. Capillary pores can be reduced, but it should be noted that gel pores will always be present when C-S-H is formed as about 34% of the C-S-H volume is gel porosity [1, 2]. This gel porosity in the paste readily follows from multiplying eq. (13) with 34%. Together with the total capillary porosity (eq. (22)), the total paste porosity is then obtained (assuming that the unhydrated cement and all other hydration products are nonporous).

6.2 Relative humidity of 80%

Substituting the CEM I composition in eqs. (15) and (16) yields

$$w_{d80}/c = 0.310 + 0.016\alpha; \quad \frac{w_{d80}\,v_d}{v_w\,c} = 0.272 + 0.013\alpha \quad , \tag{23}$$

see eq. (1) whereby $v_c/v_w = 0.32$ is invoked. Substitution of eq. (23) into eqs. (1)-(4) yield the following volume fractions

$$\varphi_{hp80} = \frac{(0.592 + 0.013\,\alpha)\,m}{0.320 + w_0/c_0} \quad ; \tag{24}$$

$$\varphi_{c80} = \frac{0.320\,(1 - m)}{0.320 + w_0/c_0} \quad ; \tag{25}$$

$$\varphi_{w80} = \frac{w_0/c_0 - (0.310 + 0.016\,\alpha)\,m}{0.320 + w_0/c_0} \qquad ; \qquad (26)$$

$$\varphi_{s80} = \frac{(0.038 + 0.003\,\alpha)\,m}{0.320 + w_0/c_0} \qquad ; \qquad (27)$$

respectively. Note that now the chemical shrinkage is about half of that of saturated paste (eq. (21)), as less "compressed" gel water is bound at 80% RH. For full hydration under sealed condition, so water cannot imbibe, $w_0/c_0 > 0.31$ is sufficient for full hydration. Though no external water imbibes, still less water is needed than under saturated hydration as at 80% RH less water is bound. But when the paste hydrates at 80% RH *and* also water vapour can imbibe (paste is not sealed), so that the volume created by chemical shrinkage can be filled, even a $w_0/c_0 = 0.272 + 0.013\alpha$ would be sufficient for complete hydration ($m = 1$). The deficiency of initial water is then compensated by external water supply, enabled by the chemical shrinkage of the system; the same feature as seen for saturated hydration with water imbibition. This might be an explanation for why Roessler and Odler ([11], "Table III") obtained full hydration at a w_0/c_0 as low as 0.22 when curing the cement paste in mist.

7 Comparison with results Taylor [6]

In Table 6 the volume and mass fractions of the different hydration products are specified, using the formulas of Tables 2 and 3, and substituting the above-mentioned CEM I composition.

In Table 6 also computations by Taylor [6] are given ("Table 7.3"), who assessed the composition of a 14 month old Portland cement paste equilibrated at 11% RH (some part of the cement was considered as unreacted). The mass of bound water is then about 30% on mass of cement. The concerned cement contained (by mass) 65.3% C, 21.0% S, 5.6% A, 3.1% F and 2.6% $\overline{S}$ (*i.e.* x_{RO} = 2.4%). Using the equations of Bogue [12], it follows that x_{C_3S} = 56.7%, x_{C_2S} = 17.5%, x_{C_3A} = 9.6%, x_{C_4AF} = 9.4% and $x_{C\overline{S}}$ = 4.4%. The composition of this cement is similar to the CEM I taken as example in the previous Section, its calcium silicates content is slightly lower, and the aluminate content in turn is higher.

Comparing the values of Table 6 it follows that some the values for C-S-H and CH are in close agreement, and that these hydration products constitute about 2/3 of the total hydration product (both in mass and volume). The quantities of the other hydration products, however, differ remarkably. Taylor [6] excludes for instance the formation of hydration product tetra calcium aluminate hydrate (C_4AH_x), which presence is also minor here, and predicts less ettringite. As a consequence more hemi-

/mono-carbonate and mono-sulphate are taken to be formed from the aluminate.

Hydration Product	m_{hp}/c	$m_{hp}/m_{hp,t}$	$m_{hp}/m_{hp,t}$ [6]	$V_{hp}/v_w c$	$V_{hp}/V_{hp,t}$
$C_6AFS_2H_{18}$	0.215	15.3 %	4.2 %	0.096	15.1 %
$C_6A\bar{S}_3H_{36}$	0.068 + 0.062 α	(4.8 + 4.1α) %	4.0 %	0.040 + 0.036 α	(6.3 + 5.0α) %
$C_4A\bar{S}H_{14}$	0.092 (1 − α)	7.0 (1 − α) %	6.8 %	0.046 (1 − α)	8.1 (1 − α) %
$C_4A\bar{C}_{0.5}H_{12}$	0.052 α	3.5α %	7.1 %	0.026 α	3.6α %
C_4AH_{22}	0.023	1.6 %	0 %	0.013	2.0 %
$C_{1.7}SH_{3.2}$	0.667	47.7 %	49.7 %	0.295	45.2 %
CH	0.295 − 0.003 α	(21.1 − 0.2α) %	19.5 %	0.132 − 0.002 α	(20.6 − 0.3α) %
UO	0.040 − 0.005 α	(2.9 − 0.4α) %	8.7 %	0.017 − 0.001 α	(2.7 − 0.2α) %
Total	1.400 + 0.014 α	100 %	100 %	0.639 + 0.013 α	100 %

Table 6 Absolute mass and volume of each hydration product relative to reacted mass of CEM I, the total being the mass and volume of the hydration product (all in saturated state, 100% RH), and the mass and volume fractions of each hydration product in the total hydration product. Note that $C_4A\bar{C}_{0.5}H_{12}$ stands for the total of hemi-carbonate ($C_4A\bar{C}_{0.5}H_{12}$) and mono-carbonate ($C_4A\bar{C}H_{11}$). Also included are the mass fractions estimated by Taylor [6].

Furthermore, the difference in mass of hydrogarnet is pronounced, which has various reasons. Firstly, Taylor [6] considers about 20% of ferrite as unreacted.
Secondly, reacted F is allowed to partly enter hemi-/mono-carbonate and mono-sulphate (which is another reason for their larger quantity). Furthermore, the formed hydrogarnet is not assigned the high water binding stage as proposed here, which reduces its mass and mass fraction in the hydration product. All these features result in the observed difference in quantity of formed hydrogarnet (Table 6).
In Table 7 the volume and mass fractions of the different hydration products at 80% RH are specified, now using the formulas of Tables 4 and 5, and substituting the above-mentioned CEM I composition. In this table also computations by Taylor [6] are given; see also the discussion above for details in this regard. Comparing the values listed in Tables 6 and 7 it follows that the quantities pertaining to 80% RH are closer to those of Taylor [6] then the ones of 100% RH.

Hydration Product	m_{hp}/c	$m_{hp}/m_{hp,t}$	$m_{hp}/m_{hp,t}$ [6]	V_{hp}/v_wc	$V_{hp}/V_{hp,t}$
$C_6AFS_2H_8$	0.178	13.6 %	4.2 %	0.059	9.8 %
$C_6A\bar{S}_3H_{32}$	0.065 + 0.058 α	(4.7 + 4.1α) %	4.0 %	0.036 + 0.033 α	(6.2 + 5.1α) %
$C_4A\bar{S}H_{12}$	0.086 (1 − α)	6.9 (1 − α) %	6.8 %	0.043 (1 − α)	8.4 (1 − α) %
$C_4A\bar{C}_{0.5}H_{12}$	0.052 α	3.6α %	7.1 %	0.026 α	4.0α %
C_4AH_{13}	0.018	1.4 %	0 %	0.009	1.5 %
$C_{1.7}SH_{2.5}$	0.628	47.9 %	49.7 %	0.296	49.3 %
CH	0.295 − 0.003 α	(22.5 − 0.3α) %	19.5 %	0.132 − 0.002 α	(22.0 − 0.4α) %
UO	0.040 − 0.005 α	(3.0 − 0.5α) %	8.7 %	0.017 − 0.001 α	(2.8 − 0.3α) %
Total	1.310 + 0.016 α	100 %	100 %	0.592 + 0.013 α	100 %

Table 7 Absolute mass and volume of each hydration product relative to reacted mass of CEM I, the total being the mass and volume of the hydration product (all at 80% RH), and the mass and volume fractions of each hydration product in the total hydration product. Note that $C_4A\bar{C}_{0.5}H_{12}$ stands for the total of hemi-carbonate ($C_4A\bar{C}_{0.5}H_{12}$) and mono-carbonate ($C_4A\bar{C}H_{11}$). Also are included the mass fractions estimated by Taylor [6].

This is no surprise as the quantities given by Taylor [6] are based on 11% RH. One can still see, however, some slight discrepancy in Table 7, the reasons for which have been discussed above.

Conclusions

Powers and Brownyard [3] presented a paste model that accounts for unreacted cement, free water, the hydration product (which is porous in itself, *i.e.* gel porosity) and chemical shrinkage (Figure 1). Careful execution of experiments resulted in quantity and specific volume of both non-evaporable water and gel water. The water retention in P-dried and saturated states was furthermore related to the clinker composition of the cement (alite, belite, aluminate and ferrite contents). Brouwers [1, 2, 8, 9] used this information develop a reaction scheme for the individual reactions of the five major cement phases: alite, belite, aluminate, ferrite and calcium sulphates. Here, this information is used to develop in a more detailed paste model, in which the composition if the hydration product is specified in more detail (Figure 1). It is also shown that this model can be used to simulate the incongruent hydration of these five major cement phases, both in saturated state and at 80% relative humidity, and at any given degree of carbonation α. In this way a relatively compact and simple

cement hydration model is obtained that can be used for engineering end purposes.

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