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The work of Powers and Brownard revisited: Part 1

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Abstract

Powers and Brownard [Studies of the physical properties of hardened Portland cement paste. Bull. 22, Res. Lab. of Portland Cement Association, Skokie, IL, U.S. *J. Am. Concr. Inst. (Proc.)*, 43 (1947) 101–132, 249–336, 469–505, 549–602, 669–712, 845–880, 933–992 (reprint)] were the first to systematically investigate the reaction of cement and water and the composition of cement paste. They introduced the concept of nonevaporable (water retained in P-dried state) and gel water (additional water retained upon saturation). Their specific volumes (v_n and v_g) are lower than that of free water, causing chemical shrinkage. The retained water was furthermore related to the content of the four most abundant clinker phases, viz alite, belite, aluminate and ferrite.

Their work is recapitulated here. Major aspects, such as the specific volume of nonevaporable and gel water, are addressed, as well as the issue of gel water being “compressed”. Subsequently, it will be demonstrated that their water retention data enable the study of the molar reactions of the calcium silicate phases and the reaction products C-S-H ($C_{1.7}SH_{3.2}$ when saturated) and CH, which represents a principal innovation. Using the molar reactions and the specific volumes of nonevaporable (v_n) and gel water (v_g), the density of saturated C-S-H and its porosity are derived.

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1. Introduction

In a pioneering work, Powers and Brownard [1] 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 model for the cement paste, in which unreacted water and cement, the reaction product and (gel and capillary) porosity were distinguished. Major paste properties were determined by extensive and carefully executed experiments, including the amount of retained water and the chemical shrinkage associated with hydration reaction. These properties were furthermore related to the content of the four most important clinker phases, viz alite, belite, aluminate and ferrite. Additionally, the composition of the cement paste was related to engineering properties, such as compressive strength, shrinkage, porosity, water permeability and freezing/thawing. Their model furthermore distinguished gel and capillary porosity. The impact of this standard work is paramount, and their concepts and results

are used in contemporary cement and concrete science [2,3]. For a historical overview of the development of Portland cement research until 1960, starting with the first publications and dissertation by Le Chatelier in 1887, the reader is referred to Steinour [4].

This paper addresses the work of Powers and Brownard for four reasons. First, although their work is widely cited (although perhaps not widely read), a rigorous review of their theoretical model and experimental results is still lacking. Taylor [2], Neville [3], Czernin [5], Locher [6], Hansen [7] and Jensen and Hansen [8] summarise the most important features of the model, but the underlying experiments, model and equations deserve a more in-depth discussion. Furthermore, these authors make use of later work by Powers [9,10], which refers to Cement 15754 to illustrate the implications of the model. This latter cement is, however, not representative of contemporary Portland cements (CEM I, corresponding to ASTM Type III cement), which contain more alite. Based on Cement 15754, the model predicts a minimum water cement ratio of 0.42 [7,8] to 0.44 [2] for complete hydration. The present analysis will reveal that this value is actually much lower for CEM I (around 0.39), being in line with values accepted nowadays. This

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aspect is a second motivation for the present analysis of their work. Third, in later publications, the work of Powers and Brownyard [1] was corrected (e.g., their prediction of chemical shrinkage) or criticized (e.g., their drying and sorption experiments). The relevance of these comments will also be addressed in the present study. Finally, and probably most importantly, it will be demonstrated that their results enable the study of the reactions of the four clinker phases and quantification of their reaction products, which is a principal innovation. A short treatment of these reactions was presented recently [11].

In the past, the model predictions have been compared with pure C_3S ¹ hydration by Locher [12] and Young and Hansen [13]. To this end, the water binding of cement as given by Powers [9] was used, i.e., the data pertaining to Cement 15754. This approach is permitted, as C_3S is a major constituent of Portland cement. The model of Powers and Brownyard [1], however, contains specific information in regard to the reaction of each individual clinker phase, such as C_3S . This aspect of their model, overlooked in the past, has been presented elsewhere recently by Brouwers [11,14] and will be analysed in detail here.

Using their model and data yields some major advantages. First, in contrast to plain clinker hydration experiments, their experiments and model are based on a real cement–water system. In contrast to hydrating pure clinker minerals, a mix of clinker minerals that contains impurities and that hydrate simultaneously is more compatible with practice. Furthermore, their experiments concerned paste hydration, which is also closer to reality than are bottle hydration experiments that are frequently reported. Applying their work to the hydration of the calcium silicate phases yields the reaction stoichiometry, as well as the amount, density, porosity, water content, etc. of the most abundant reaction product, C-S-H. Likewise, in the approach of Le Chatelier, a picture that is generally accepted nowadays, the calcium silicate phases are assumed to react independently from the aluminate phase [4]. In a future publication [15], it will be seen that the work of Powers and Brownyard [1] can also be applied to the reactions of aluminate, ferrite and sulphate phases. The type of products formed and their quantities can be derived from their water retention data. Their classical work contains much more information and will have a wider application than is generally appreciated.

2. Theory

In this section, the main features of the model by Powers and Brownyard [1] are recapitulated. The terms and symbols used are, as much as possible, consistent with theirs, as well as those used in later work by Powers [9,10,16–18].

Powers and Brownyard [1] distinguished three phases in the cement paste viz capillary water (=unreacted water), unreacted cement and cement gel (Fig. 1). The cement gel consists of solid hydrated cement and water-filled gel pores; this water is referred to as gel or absorbed water. The gel water is visualised as being within the influence of absorbing forces, whereas the capillary water is considered as “free water”. Like Taylor [2], the term “hydration product” is used instead of “gel” to avoid confusion in regard to “gel” and “gel water”. Hence, here, the hydration product consists of hydrated cement and gel space, whereby the latter may be filled with gel water.

2.1. Definitions

The hydrated cement thus consists of reacted cement and the nonevaporable water, also termed “water of constitution” or “chemically combined water”. The volume of the hydrated cement is expressed in the volume of the reacted cement and by assigning a specific volume to the reacted water:

$$V_{hc} = v_c c + w_n v_n \quad (1)$$

where c is the mass of reacted cement (in a later publication by Powers [9], the special symbol c_h was also introduced). Note that the volume change involved with this reaction is accounted for by assigning a specific volume (density) to the water reacted. The volume of the hydration product comprises the hydrated cement and the gel water:

$$V_{hp} = V_{hc} + w_g v_g = c v_c + w_n v_n + w_g v_g = c v_c + w_d v_d. \quad (2)$$

This gel water is also assigned a specific volume, as it differs from free water. The specific volumes of both nonevaporable (v_n) and gel water (v_g) were considered to be lower than that of free water and both designated as

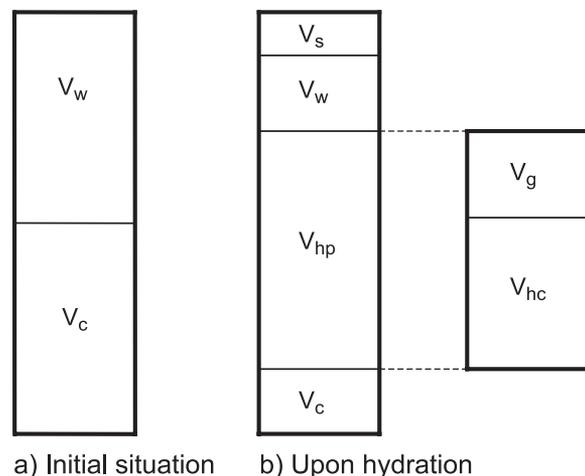


Fig. 1. Breakdown of cement paste and hydration product ($m=0$ and $m>0$).

¹ Cement chemistry notation is employed: C=CaO, S=SiO₂, etc.

“compressed water”. The mass of compressed water thus comprises:

$$w_d = w_n + w_g. \quad (3)$$

The specific volume of all compressed water follows from

$$v_d = \frac{w_n v_n + w_g v_g}{w_n + w_g} = \frac{w_n v_n + w_g v_g}{w_d}, \quad (4)$$

whereby Eq. (3) has been inserted. The specific volume of all water follows from

$$v_t = \frac{w_c v_w + w_n v_n + w_g v_g}{w_c + w_n + w_g} = \frac{w_c v_w + w_d v_d}{w_c + w_d}, \quad (5)$$

in which the capillary water mass, w_c , has been introduced. The sum of capillary water and gel water is also referred to as evaporable water:

$$w_e = w_c + w_g. \quad (6)$$

The volume of the unreacted (or anhydrous) cement is

$$V_c = (c_0 - c)v_c = (1 - m)c_0 v_c. \quad (7)$$

In which the concept of maturity is introduced, defined as

$$c = mc_0, \quad (8)$$

nowadays more usually called “hydration degree”. It is an overall property, although the plain clinker phases may have different reaction rates. Joined in cement, these minerals react, however, more congruently, and for hydration degrees above 50%, this overall hydration degree serves well to define the degree of reaction of each clinker phase [19,20].

Powers and Brownyard [1] referred to the total solid phase either as “ V_s ”, which follows from adding V_{hc} and V_c (yielding $c_0 v_c + w_n v_n$) or as “ V_b ”, which also includes the gel water space, i.e., comprising $V_{hp} + V_c (= c_0 v_c + w_n v_n + w_g v_g = c_0 v_c + w_d v_d$; see Fig. 1).

The volume of the pore water follows from

$$V_w = (w_0 - w_d)v_w = (w_0 - w_n - w_g)v_w. \quad (9)$$

The total volume of the water and cement becomes

$$V_t = c_0 v_c + w_0 v_w. \quad (10)$$

So that as volume shrinkage of the system is

$$\begin{aligned} V_s &= V_t - V_{hp} - V_c - V_w = w_n(v_w - v_n) + w_g(v_w - v_g) \\ &= w_d(v_w - v_d). \end{aligned} \quad (11)$$

The total capillary pore volume follows from adding Eqs. (9) and (11):

$$\begin{aligned} V_{cp} &= V_w + V_s = w_0 v_w - w_n v_n - w_g v_g \\ &= w_0 v_w - w_d v_d. \end{aligned} \quad (12)$$

Under dry conditions, V_s will be filled with air and /or vacuum, and hence, the total water in the system follows from

$$w_t = w_0, \quad (13)$$

that is, the total water equals the initial mixing water. In a paste that hardens under saturated conditions, this volume will be filled with external water; in that case V_w becomes equal to V_{cp} , and the total water mass of the system will increase by imbibition and follows from Eq. (11) as:

$$w_t = w_0 + \frac{V_s}{v_w} = w_0 + \frac{w_d(v_w - v_d)}{v_w}. \quad (14)$$

The total water in the system is also related to the initial cement content of the system, and Eq. (14) is then divided by c_0 :

$$\frac{w_t}{c_0} = \frac{w_0}{c_0} + m \left[\frac{w_d}{c} - \frac{w_d v_d}{v_w c} \right], \quad (15)$$

whereby Eq. (8) has been inserted. From this equation, one can see that the total mass of the paste increases with increasing degree of hydration when external water may enter the paste.

Note that the imbibed water is accounted for by the second term on the right-hand side of Eq. (15), and that this water increases the amount of capillary water, w_c . Furthermore, one can derive the maximum achievable maturity as:

$$m \leq \frac{\frac{w_t}{c_0}}{\frac{w_d}{c}}, \quad (16)$$

with $m = 1$ in case the right hand-side exceeds unity. Using Eqs. (13) and (14), the maximum maturity follows from

$$m \leq \frac{\frac{w_0}{c_0}}{\frac{w_d}{c}} \text{ and } m \leq \frac{\frac{w_0}{c_0}}{\frac{w_d v_d}{v_w c}}, \quad (17)$$

for sealed and saturated hydration, respectively. From Eq. (17) and considering that $v_d < v_w$, it follows that the amount of initial water can be smaller than the water needed for complete hydration, w_d , owing to the inflow of external water by shrinkage. Physically, this implies that to achieve complete hydration ($m = 1$), upon mixing, less water is required than w_d/c , as the paste will imbibe the missing water by the internal volume that is created by shrinkage (imbibed water mass). The mass of imbibed water is related to the mass of cement and is:

$$\frac{V_s}{v_w c} = \frac{w_d}{c} - \frac{w_d v_d}{v_w c}. \quad (18)$$

Now, we are in a position to define some important physical properties of gel and paste. The specific volume of the hydrated cement reads

$$v_{hc} = \frac{cv_c + w_n v_n}{c + w_n} = \frac{v_c + (w_n/c)v_n}{1 + w_n/c}. \quad (19)$$

The bulk volume of the hydration product in saturated state (including gel water) follows from

$$\begin{aligned} v_{hp} \text{ (saturated)} &= \frac{cv_c + w_n v_n + w_g v_g}{c + w_n + w_g} = \frac{cv_c + w_d v_d}{c + w_d} \\ &= \frac{v_c + (w_d/c)v_d}{1 + (w_d/c)} \end{aligned} \quad (20)$$

and in P-dried condition (gel water removed),

$$\begin{aligned} v_{hp} \text{ (P-dried)} &= \frac{cv_c + w_n v_n + w_g v_g}{c + w_n} = \frac{cv_c + w_d v_d}{c + w_n} \\ &= \frac{v_c + (w_d/c)v_d}{1 + (w_n/c)}. \end{aligned} \quad (21)$$

The porosity of (or gel space in) the hydration product follows from

$$\begin{aligned} \Phi_g &= \frac{w_g v_g}{cv_c + w_n v_n + w_g v_g} = \frac{w_g v_g}{cv_c + w_d v_d} \\ &= \frac{(w_g/c)v_g}{v_c + (w_d/c)v_d}. \end{aligned} \quad (22)$$

The P-dried density of the hydration product, which corresponds to the bulk density of hydrated cement, is related to the density of the hydrated cement (i.e., its intrinsic density) and the porosity of the hydration product via

$$\rho_{hp} \text{ (P-dried)} = (1 - \Phi_g)\rho_{hc}, \quad (23)$$

which can easily be verified by combining Eqs. (20) and (22) and using $\rho = 1/v$. The volume of total porosity of the paste comprises the capillary porosity and the porosity of the hydration product (its gel volume). This gel volume is obtained by multiplying Φ_g and V_{hp} , hence:

$$V_{tp} = V_{cp} + \Phi_g V_{hp} = w_0 v_w - w_n v_n, \quad (24)$$

see Eqs. (2), (12), and (22). V_{tp} constitutes, in fact, the initial volume of the water minus the volume of the nonevaporable water, i.e., only this water is considered not to be part of the porosity.

2.2. Volume fractions

The volume fraction of hydration product in the cement paste follows from Eqs. (2) and (10):

$$\varphi_{hp} = \frac{V_{hp}}{V_t} = \frac{m \left[\frac{V_{hp}}{v_w c} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{m \left[\frac{v_c}{v_w} + \frac{w_d v_d}{v_w c} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}}, \quad (25)$$

whereby Eq. (8) has been inserted. The volume fraction of the unreacted cement follows from Eqs. (7), (8) and (10) as

$$\varphi_c = \frac{V_c}{V_t} = \frac{(1-m) \left[\frac{v_c}{v_w} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} \quad (26)$$

and of the unreacted water from Eqs. (8)–(10) as

$$\varphi_w = \frac{V_w}{V_t} = \frac{\frac{V_w}{v_w c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{\frac{w_0 - w_d}{c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{w_0 - m \left[\frac{w_d}{c} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} \quad (27)$$

and the shrinkage volume part from Eqs. (8), (10) and (11) as

$$\varphi_s = \frac{V_s}{V_t} = \frac{\frac{V_s}{v_w c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{\frac{w_d}{v_w} - \frac{w_d v_d}{v_w c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = m \left[\frac{\frac{w_d}{c} - \frac{w_d v_d}{v_w c}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} \right]. \quad (28)$$

It readily follows that $\varphi_c + \varphi_{hp} + \varphi_w + \varphi_s = 1$, thus, the total paste volume is completely comprised by these four fractions. The total-capillary-pore fraction φ_{cp} amounts to $\varphi_w + \varphi_s$ and follows from Eqs. (27) and (28) as

$$\varphi_{cp} = \frac{V_{cp}}{V_t} = \frac{V_w + V_s}{V_t} = \frac{\frac{w_0 - w_d v_d}{c_0} - \frac{w_d v_d}{v_w c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{w_0 - m \left[\frac{w_d v_d}{v_w c} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}}, \quad (29)$$

which is also called capillary porosity of the paste. As stated before, under saturated conditions, φ_{cp} is filled with water if access is possible. With limited access or under sealed conditions, it is partly filled with water and partly with air/vacuum. Thus, the capillary pore space is the remnant of the initial mixing water that exists between the cement phase and the space created by chemical shrinkage. Under saturated conditions, and considering the second expression of Eqs. (17), (29) may yield $\varphi_{cp} = 1$; that is, all volume is occupied by the hydration product. This is not possible when water has no free access or sealed hydration takes place, this follows from the first expression of Eq. (17).

In addition, a total porosity of the cement paste can be defined, being the sum of capillary and gel porosity:

$$\varphi_{tp} = \frac{V_{cp} + \Phi_g V_{hp}}{V_t} = \frac{\frac{w_0 - w_n v_n}{c_0} - \frac{w_n v_n}{v_w c_0}}{\frac{v_c}{v_w} + \frac{w_0}{c_0}} = \frac{w_0 - m \left[\frac{w_n v_n}{v_w c} \right]}{\frac{v_c}{v_w} + \frac{w_0}{c_0}}, \quad (30)$$

whereby Eqs. (2), (8), (10), (12) and (22) have been substituted.

Eqs. (25)–(30) contain the maturity, which depends on type of cement, hydration time, hardening conditions etc.,. For many types of cement, m can be estimated, as well as the specific volume of the cement ($v_c \approx 0.32 \text{ cm}^3/\text{g}$ or $\rho_c \approx 3.125 \text{ g/cm}^3$). Eqs. (25)–(30) also contain the mass of retained nonevaporable water per mass of hydrated cement (w_n/c), gel water per mass of hydrated cement (w_g/c) and the

specific volumes of nonevaporable (v_n) and gel water (v_g). It will be demonstrated that w_n/c , w_g/c and its total, w_d/c , are constant in time and depend on cement composition. The appearing capillary water can be assigned a specific volume of $1 \text{ cm}^3/\text{g}$. To apply the model of Powers and Brownyard [1], the nonevaporable (w_n/c) and gel water (w_g/c) and their specific volumes need to be known. These specific volumes govern the volume fractions of unreacted cement, hydration product (and its gel porosity), unreacted (capillary) water and the shrinkage of the paste. In the next section, these properties will be specified.

3. Water retention and shrinkage

As said, the model as discussed in the previous section requires quantification of nonevaporable and gel water, as well as their specific volumes. To this end, Powers and Brownyard [1] executed and reported numerous experiments with cements of different compositions, with neat cement and with mortars, and at various water/cement ratios (w_0/c_0) and various hardening times. Most mixtures were cured at $21.1 \text{ }^\circ\text{C}$ ($70 \text{ }^\circ\text{F}$), but a few mixtures were steam cured in an autoclave at $215.5 \text{ }^\circ\text{C}$ ($420 \text{ }^\circ\text{F}$). Here, attention is restricted to the pastes hardened at room temperature, which were stored in water (until age of 28 days) and in a fog room (beyond 28 days). Although some precautions were taken (e.g., during the sorption experiments), the mixing took place in open air, and the water was not free from carbon dioxide. Indeed, some carbonation (pp. 253, 257, 258, 263, 269) did occur. The samples were stored in water that was frequently replenished (to avoid build up of alkalis; p. 254), and this water was not free from CO_2 either. In addition, the weathering of the cements could not be prevented (p. 492). Weathering during grinding and storage of cement will result in the formation of CaCO_3 , which is a major source of CO_2 [2]. Table A-2 (p. 305–307) gives the free lime and CO_2 contents of some cements employed [1].

Table 1 lists 39 cements, which will be used here to illustrate and extend the model, taken from Powers and Brownyard (Ref. [1], Table A-2, p. 305–307). These cements have been selected as they represent wide variations in composition. The specific volume of these cements, v_c , was about $0.32 \text{ cm}^3/\text{g}$ ($0.316\text{--}0.322 \text{ cm}^3/\text{g}$), and the (“Wagner”) specific surface was $1610\text{--}2045 \text{ cm}^2/\text{g}$ (Ref. [1], Table A-3 on pp. 308 and 309). Here, a uniform value of $v_c = 0.32 \text{ cm}^3/\text{g}$ is employed for all 39 cements. Later on, however, when the individual clinker phases are considered, their actual densities will be employed (Table 2). Note that the aforesaid Wagner specific surface is much smaller than the true specific surface, as measured with contemporary air permeability methods such as Blaine [2]. Powers and Brownyard (Ref. [1], p. 491) also found with Wagner, $1890 \text{ cm}^2/\text{g}$, and with air permeability, $3500 \text{ cm}^2/\text{g}$. Accordingly, their cements had Blaine surfaces of $3200\text{--}4100 \text{ cm}^2/\text{g}$.

The quantity of the four major clinker phases of all cements is given as well, as well as the $\text{C}\bar{\text{S}}$ content; most likely, Powers and Brownyard [1] assigned all chemical sulphate to the calcium oxide. In Table 1, the mass fraction of the remaining oxides (RO) is also included, defined as

$$x_{\text{RO}} = 1 - x_{\text{C}_3\text{S}} - x_{\text{C}_2\text{S}} - x_{\text{C}_3\text{A}} - x_{\text{C}_4\text{AF}} - x_{\text{C}\bar{\text{S}}}. \quad (31)$$

These RO comprise the alkalis (K_2O , Na_2O), MgO , free CaO , LOI , CO_2 , FeO , TiO_2 and P_2O_5 ([1], Table A-2, p. 305–307). One can readily see that the RO constitute only a minor part of the total cement mass, typically $1.4\text{--}7.1\%$.

To enable the application of the model of Powers and Brownyard [1] to contemporary cements, which are richer in alite, Table 1 also includes a typical composition of CEM I² (corresponding to ASTM Type III cement).

3.1. Nonevaporable water

For determining the nonevaporable water (w_n) P-drying was selected, although they compared several drying methods (P-drying, D-drying, drying over P_2O_5 and drying over H_2SO_4). The water that can be removed by P-drying (using vacuum and magnesium perchlorate hydrate at $23 \text{ }^\circ\text{C}$) was designated evaporable water, including gel and capillary water. During D-drying (an environment of dry ice at $-79 \text{ }^\circ\text{C}$ under vacuum), a 16 times lower water-vapour pressure is imposed (about $0.5 \times 10^{-3} \text{ mm Hg} \approx 0.67 \text{ Pa}$) than during P-drying (about $8 \times 10^{-3} \text{ mm Hg} \approx 10.7 \text{ Pa}$), resulting in about 8% less nonevaporable water compared with P-drying [9,10,21]. The D-drying method has become more popular since the second half of the 1950s (viz Copeland et al. [19]). Powers and Brownyard [1] noted that drying over P_2O_5 is even harsher; the vapour pressure is more than 100 times lower than upon P-drying. Thus, P-drying was used, and the remaining nonevaporable water was calculated as chemically bound water. This combined water can only be removed by ignition. Powers and Brownyard [1] realized, however, that not only the colloidal hydrates formed by C_3S and C_2S hydration lose water on P-drying, but that the microcrystalline reaction products of the alumina-bearing compounds can also lose “water of crystallization” (pp. 257–263).

It was noticed that w_n mainly depends on the clinker composition of the cements and the amount of reacted cement (c). Furthermore, w_n/c is almost constant in time, supporting the idea that all clinker phases hydrate in a similar rate (previous section). Table 1 shows the measured amount of nonevaporable water for the cements following 126–479 days curing and $0.437 < w_0/c_0 < 0.611$ (Ref. [1], Tables 2–6 on pp. 596–600). For all cements, the selected data reflect the longest hardening time and the highest w_0/c_0 , so that complete hydration is approximated as much as possible.

² The major condition for CEM I is that $x_{\text{C}_3\text{S}} + x_{\text{C}_2\text{S}} \geq 2/3$.

Table 1
Composition of cements, nonevaporable water (w_n/c), gel water ($w_g/c=4V_m/c$) and total retained water (w_d/c), both experimental values and fitted values (Eqs. (32), (36) and (38)), all taken from Powers and Brownyard [1]

Cement type	x_{C_2S}	x_{C_3S}	x_{C_3A}	x_{C_4AF}	x_{CS}	x_{RO}	w_n/c exp.	w_n/c fit	w_g/c exp.	w_g/c fit	w_d/c exp.	w_d/c fit	V_s^a ρ_{w^c}	V_s^b ρ_{w^c}	w_d/c (41)	v_{hc} (cm ³ /g)	v_{hp} (cm ³ /g) (saturated)	v_{hp} (cm ³ /g) (P-dried)	Φ_g
13721	0.500	0.227	0.125	0.066	0.0306	0.051	0.2231	0.227	0.253	0.228	0.477	0.455	0.086	0.063	0.467	0.394	0.473	0.561	0.298
13722	0.448	0.263	0.127	0.066	0.0306	0.065	0.2332	0.224	0.247	0.225	0.480	0.449	0.085	0.063	0.466	0.393	0.472	0.559	0.297
13723	0.470	0.252	0.118	0.066	0.0306	0.063	0.2290	0.220	0.239	0.221	0.468	0.441	0.084	0.062	0.457	0.392	0.470	0.555	0.293
13730	0.599	0.093	0.012	0.208	0.0306	0.057	0.1786	0.179	0.193	0.177	0.371	0.356	0.068	0.050	0.358	0.381	0.449	0.516	0.262
13731	0.423	0.230	0.017	0.204	0.0306	0.095	0.1772	0.170	0.170	0.171	0.347	0.341	0.065	0.048	0.355	0.378	0.445	0.510	0.258
13732	0.526	0.142	0.013	0.216	0.0306	0.072	0.1773	0.175	0.179	0.175	0.356	0.351	0.067	0.049	0.357	0.380	0.447	0.514	0.261
13736	0.590	0.158	0.105	0.090	0.0306	0.026	0.2148	0.224	0.236	0.227	0.451	0.451	0.085	0.063	0.455	0.393	0.472	0.560	0.298
13737	0.560	0.178	0.107	0.092	0.0306	0.032	0.2297	0.224	0.255	0.227	0.484	0.450	0.085	0.063	0.456	0.393	0.472	0.560	0.298
13738	0.564	0.176	0.105	0.092	0.0306	0.032	0.2220	0.223	0.224	0.226	0.446	0.448	0.085	0.062	0.454	0.393	0.472	0.559	0.297
13740	0.450	0.247	0.145	0.070	0.0306	0.057	0.2395	0.235	0.273	0.239	0.513	0.473	0.090	0.066	0.488	0.396	0.478	0.570	0.305
13741	0.460	0.240	0.144	0.070	0.0306	0.055	0.2390	0.235	0.247	0.238	0.486	0.473	0.090	0.066	0.487	0.396	0.478	0.570	0.305
13752	0.596	0.157	0.042	0.149	0.0306	0.025	0.1864	0.196	0.215	0.200	0.401	0.396	0.075	0.055	0.395	0.386	0.459	0.536	0.281
13753	0.615	0.154	0.037	0.136	0.0306	0.027	0.1896	0.193	0.212	0.195	0.402	0.388	0.073	0.054	0.387	0.385	0.457	0.532	0.276
13763	0.474	0.252	0.099	0.088	0.0306	0.056	0.2173	0.213	0.239	0.216	0.456	0.429	0.081	0.060	0.442	0.390	0.467	0.550	0.291
13764	0.417	0.294	0.099	0.088	0.0306	0.071	0.2109	0.209	0.218	0.212	0.429	0.421	0.080	0.059	0.438	0.389	0.465	0.547	0.289
13765	0.424	0.289	0.099	0.088	0.0306	0.069	0.2201	0.210	0.221	0.213	0.441	0.422	0.080	0.059	0.439	0.389	0.466	0.548	0.289
13766	0.470	0.265	0.120	0.076	0.0306	0.038	0.2096	0.226	0.237	0.234	0.447	0.460	0.087	0.063	0.469	0.394	0.475	0.565	0.304
13767	0.450	0.278	0.120	0.076	0.0306	0.045	0.2256	0.224	0.256	0.232	0.482	0.456	0.086	0.063	0.467	0.393	0.474	0.564	0.302
13768	0.457	0.273	0.120	0.076	0.0306	0.043	0.2250	0.225	0.249	0.232	0.474	0.457	0.086	0.063	0.468	0.393	0.474	0.564	0.303
13778	0.575	0.122	0.131	0.115	0.0306	0.026	0.2308	0.238	0.245	0.243	0.475	0.482	0.091	0.067	0.485	0.397	0.480	0.574	0.308
13779	0.530	0.155	0.131	0.115	0.0306	0.038	0.2329	0.235	0.225	0.240	0.458	0.475	0.090	0.066	0.482	0.396	0.478	0.571	0.306
13780	0.533	0.153	0.131	0.115	0.0306	0.037	0.2262	0.235	0.228	0.241	0.454	0.476	0.090	0.066	0.482	0.396	0.478	0.571	0.307
14900	0.492	0.225	0.122	0.097	0.0088	0.055	0.2274	0.229	0.231	0.238	0.458	0.467	0.088	0.064	0.469	0.395	0.477	0.569	0.306
14906	0.494	0.213	0.132	0.096	0.0060	0.059	0.2344	0.234	0.251	0.243	0.486	0.477	0.090	0.066	0.478	0.396	0.479	0.573	0.309
14909	0.413	0.296	0.121	0.103	0.0088	0.058	0.2255	0.226	0.242	0.241	0.467	0.467	0.087	0.063	0.470	0.394	0.477	0.571	0.310
14910	0.425	0.280	0.123	0.106	0.0088	0.057	0.2282	0.228	0.236	0.242	0.464	0.470	0.088	0.064	0.472	0.394	0.478	0.572	0.310
14911	0.396	0.301	0.132	0.107	0.0082	0.056	0.2294	0.232	0.240	0.249	0.470	0.482	0.090	0.065	0.484	0.395	0.480	0.578	0.315
14912	0.408	0.296	0.130	0.104	0.0082	0.054	0.2252	0.232	0.249	0.248	0.474	0.480	0.090	0.065	0.481	0.395	0.480	0.577	0.315
14915	0.393	0.308	0.117	0.102	0.0130	0.067	0.2240	0.222	0.240	0.234	0.464	0.455	0.085	0.062	0.463	0.393	0.474	0.565	0.305
14930	0.227	0.558	0.061	0.098	0.0264	0.030	0.2101	0.192	0.263	0.220	0.473	0.412	0.076	0.054	0.424	0.384	0.465	0.550	0.302
15007	0.480	0.291	0.068	0.105	0.0222	0.034	0.2131	0.203	0.241	0.214	0.454	0.418	0.078	0.057	0.420	0.388	0.465	0.548	0.293
15011	0.451	0.291	0.067	0.105	0.0243	0.062	0.2136	0.197	0.227	0.203	0.441	0.400	0.075	0.055	0.410	0.386	0.460	0.538	0.283
15013	0.390	0.290	0.140	0.070	0.0300	0.080	0.2447	0.227	0.234	0.229	0.479	0.456	0.086	0.063	0.477	0.394	0.474	0.562	0.299
15365	0.450	0.280	0.133	0.067	0.0420	0.028	0.2546	0.231	0.239	0.240	0.494	0.471	0.089	0.065	0.485	0.395	0.478	0.571	0.308
15754	0.450	0.277	0.134	0.067	0.0400	0.032	0.2301	0.231	0.230	0.240	0.460	0.471	0.089	0.065	0.485	0.395	0.477	0.570	0.307
15756	0.486	0.279	0.047	0.126	0.0290	0.033	0.1684	0.193	0.180	0.203	0.348	0.396	0.074	0.054	0.400	0.385	0.460	0.538	0.284
15758	0.606	0.116	0.102	0.077	0.0320	0.067	0.2227	0.216	0.217	0.205	0.440	0.421	0.081	0.060	0.434	0.391	0.464	0.543	0.279
15761	0.449	0.292	0.098	0.075	0.0310	0.055	0.2120	0.211	0.220	0.216	0.432	0.427	0.081	0.059	0.441	0.390	0.467	0.550	0.291
15763	0.335	0.536	0.023	0.060	0.0320	0.014	0.1487	0.175	0.180	0.195	0.329	0.370	0.069	0.049	0.382	0.380	0.454	0.529	0.282
CEM I	0.610	0.150	0.060	0.100	0.0400	0.040		0.199		0.194		0.393	0.075	0.056	0.402	0.386	0.458	0.532	0.274

^a $v_c=0.32$ cm³/g, $v_w=1$ cm³/g, $v_n=0.72$ cm³/g and $v_g=0.9$ cm³/g.

^b $v_c=0.32$ cm³/g, $v_w=1$ cm³/g, $v_n=0.72$ cm³/g and $v_g=1$ cm³/g.

Table 2
Properties of compounds

Substance	M (g/mol)	ρ (g/cm ³)	ω (cm ³ /mol)
C ₃ S	228.33	3.120	73.18
C ₂ S	172.25	3.326	51.79
C ₃ A	270.20	3.060	88.30
C ₄ AF	485.97	3.730	130.29
C \bar{S}	136.14	2.558	53.22
C \bar{S} H _{0.5}	145.15	2.733	53.11
C \bar{S} H ₂	172.18	2.310	74.54
C \bar{C}	100.09	2.711	36.92
H	18.02	1.000	18.02
CH	74.10	2.242	33.05
C _{1.7} SH _{3.2}	213.09	2.253	94.60
C _{1.7} SH _{1.2}	177.05	2.856	62.00

Densities are based on XRD data from Taylor [2], the properties of C_{1.7}SH_{1.2} and C_{1.7}SH_{3.2} are based on the present work.

Being aware that larger cement particles had not reacted fully, the Powers and Brownyard [1] fitted the following relation between w_n/c and the clinker composition:

$$w_n/c = 0.187 x_{C_3S} + 0.158 x_{C_2S} + 0.665 x_{C_3A} + 0.213 x_{C_4AF}. \quad (32)$$

In Table 1, the w_n/c , as computed by Eq. (32), has been included, and it can be readily seen that the agreement with the experimental values is good and that complete hydration was closely attained during the selected experiments.

Eq. (32) expresses the mass of retained water (upon P-drying) per mass of reacted cement as a function of the clinker phase composition of the cement. This equation can be expressed as moles of retained water per mole of reacted clinker phase via the relation

$$m_{C_3S} = x_{C_3S} c; \quad m_{C_2S} = x_{C_2S} c; \quad \text{etc.}, \quad (33)$$

$$w = M_H n_H; \quad m_{C_3S} = M_{C_3S} n_{C_3S}; \quad m_{C_2S} = M_{C_2S} n_{C_2S}; \quad \text{etc.}, \quad (34)$$

yielding

$$n_{H,n} = 2.37 n_{C_3S} + 1.51 n_{C_2S} + 9.97 n_{C_3A} + 5.74 n_{C_4AF}, \quad (35)$$

whereby the molecular masses of the clinker phases are taken from Table 2.

The nonevaporable water has also been determined by Copeland et al. [19], using both P- and D-drying for pastes matured for 1, 6.5 and 13 years. In Table 3, the coefficients of Copeland et al. [19] (by P-drying) are summarised. A glance at this table and Eq. (32) reveals that the nonevaporable water for the C₃S and C₂S is quite similar,

but for the C₃A and C₄AF reactions, deviating values are reported.

3.2. Gel water

Powers and Brownyard [1] used the P-dried samples to perform sorption experiments using water vapour. They found that at a relative humidity below 45%, the amount of water held is proportional to the amount of cement reacted and, hence, the amount of gel formed. Above this relative humidity, the water also condenses in the larger capillary pores. When the pores are modelled as cylindrical tubes, and assuming that only tubes with a radius smaller than the meniscus curvature pertaining to the aforesaid relative vapour pressure are filled, the threshold diameter of gel to capillary pores thus takes a value of about 2.7 nm (Ref. [1], p. 475). The cement samples were flushed to remove alkalis, as it was recognised that alkalis reduce the water vapour pressure.

Furthermore, applying the B.E.T. theory to the measured adsorption isotherm, a quantity V_m was measured corresponding to the mass of water necessary to cover the hydrated cement with one monolayer. This first layer was obtained at a relative humidity of about 20%. From the experiments, it was furthermore concluded that the maximum amount of water that can be retained by the hydration product, i.e., gel water, corresponds to $4V_m$ per mass of reacted cement. This water quantity is retained at saturation (Fig. 2), and water surplus to $4V_m$ is capillary water (Fig. 3). This result was explained by the concept that V_m is the mass of water necessary to cover the hydrated cement in the hydration product with one layer of water, and that with four layers, the hydration product (gel space) is saturated. Based on a large number of carefully executed sorption experiments, Hagymassy et al. [22] measured that the amount absorbed at saturation is 4–5 times the amount adsorbed at a relative pressure of 20%, and that at saturation five to six water layers are adsorbed; this is compatible with the finding of Powers and Brownyard [1].

Powers and Brownyard [1] furthermore observed that V_m is linearly proportional to the amount of nonevaporable water. This was explained by the fact that the internal surface of the hydration product is proportional to the amount of cement reacted. In a later work, Brunauer and Kantro [23] experimentally confirmed for C₂S and C₃S hydration that the surface development

Table 3
Coefficients to be used in Eq. (32) to determine chemically bound water following Copeland et al. [19]

Age (years)	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
1	0.228	0.168	0.429	0.132
6.5	0.234	0.178	0.504	0.158
13	0.230	0.196	0.522	0.109

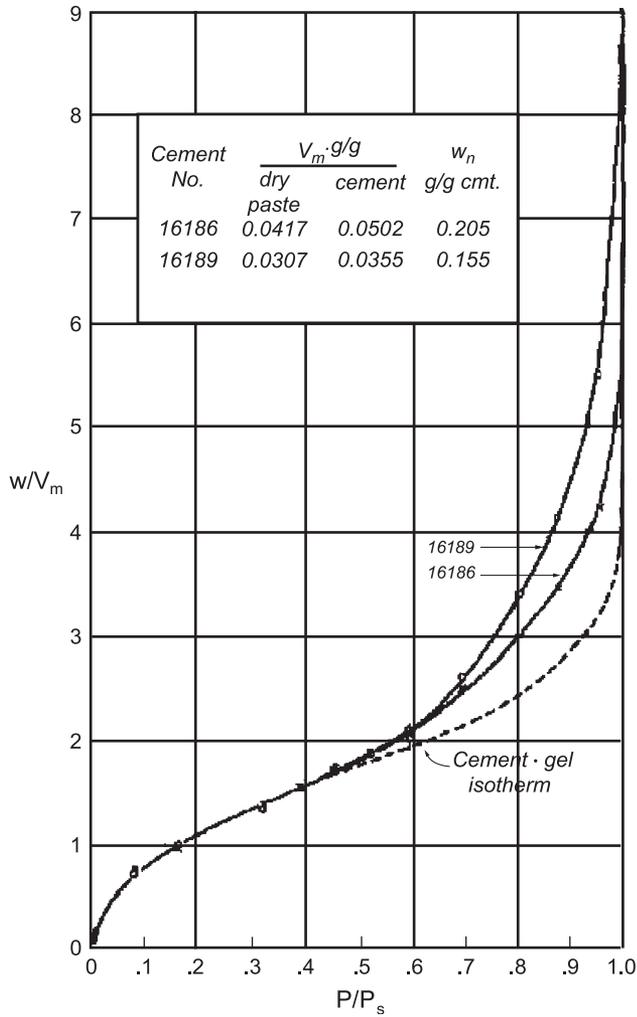


Fig. 2. w_g/V_m vs. relative humidity for the cement samples used in heat of adsorption measurements (Fig. 4-2, taken from p. 554, Ref. [1]).

closely follows the degree of hydration indeed. In view of this direct relation, Powers and Brownyard [1] introduced and measured the property V_m/w_n , which was referred to as k , accordingly:

$$w_g/w_n = B' = 4k = 4V_m/w_n. \tag{36}$$

In Table 1, the measured w_g/c for the listed cements are included (obtained by multiplying the measured $4V_m/w_n$ and w_n/c). These values are taken from Ref. [1] (Tables 2–6, pp. 596–600).

Furthermore, it was recognised that the amount of internal surface (i.e., the amount and type of hydration products) depends on the composition of the cement. Powers and Brownyard [1] therefore recommended the following empirical fit:

$$V_m/w_n = 0.230 x_{C_3S} + 0.320 x_{C_2S} + 0.317 x_{C_3A} + 0.368 x_{C_4AF}. \tag{37}$$

For the cements listed in Table 1, the fit of w_g/c has been computed using Eqs. (32) and (37), and the computed values are included in Table 1 as well.

The fitted and measured values are in good agreement, but the agreement is less good than between the measured and fitted values of w_n/c (Table 1). The constancy of w_g/w_n for a given cement is not a trivial result and supports the viewpoint (previous section) that the fractional rate of hydration of the clinker phases is approximately the same. Each clinker phase produces hydration products with their own retention of gel water; it can be concluded that all phases hydrate more or less congruently.

In Table 1, w_d/c is also included, both measured and computed, following from Eqs. (3) and (36) as

$$w_d/c = (1 + B') w_n/c = B w_n/c. \tag{38}$$

Comparing w_d/c and w_n/c (the difference is w_g/c), one can conclude that the amount of gel water is almost equal to the amount of nonevaporable water ($B' \approx 1$).

The amount of retained water per clinker phase can be obtained by substituting $x_{C_3S} = 1$ ($c = m_{C_3S}$), $x_{C_2S} = 1$ ($c = m_{C_2S}$), etc. into Eqs. (32) and (36)–(38), yielding:

$$w_d = 0.359 m_{C_3S}, \quad w_d = 0.360 m_{C_2S}, \quad w_d = 1.508 m_{C_3A}, \\ w_d = 1.016 m_{C_4AF}, \tag{39}$$

respectively. This result can be written in moles of water per mole of clinker phase using Eq. (34)

$$n_{H,d} = 4.55 n_{C_3S}, \quad n_{H,d} = 3.44 n_{C_2S}, \quad n_{H,d} = 22.6 n_{C_3A}, \\ n_{H,d} = 14.2 n_{C_4AF}. \tag{40}$$

As said, Powers and Brownyard [1] have expressed the gel water in the nonevaporable water. It enables the coupling

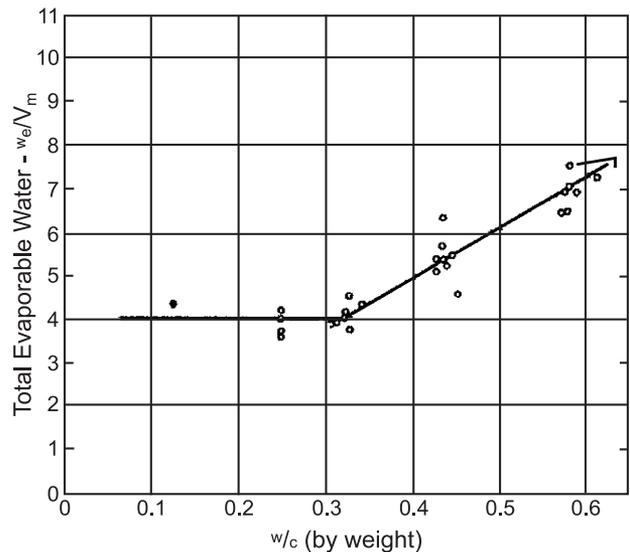


Fig. 3. Empirical relationship between total evaporable water per unit V_m and original water–cement ratio for samples cured 180 days or longer (Fig. 3.13, taken from p. 502, Ref.[1]).

of gel water (and hence, total retained water) to nonevaporable water, also when complete hydration is not attained (i.e., the actual w_n/c being smaller than w_n/c required for complete hydration, e.g., as predicted by Eq. (32)). For a pure clinker phase, the total retained water can be expressed in the mass of or moles of such phase (by substituting $x=1$ into Eqs. (32) and (37)). For cements that consist of several clinker phases, w_d can, however, not be expressed in terms of the mass fraction and number of moles of clinker phases (likewise, Eq. (32)), which is a disadvantage of the chosen approach. Furthermore, the total retained water could also depend on the $C\bar{S}H_2$ content, thus, it is desirable to include this mass fraction in a fit as well. Accordingly, a least-squares method is employed to the experimental data of Table 1 to obtain

$$w_d/c = 0.334 x_{C_3S} + 0.374 x_{C_2S} + 1.410 x_{C_3A} + 0.471 x_{C_4AF} + 0.261 x_{C\bar{S}}. \quad (41)$$

Likewise, as for the nonevaporable water, for the saturated state, now, the retained moles of water can be expressed in moles of the clinker phases as well using Eqs. (33) and (34)

$$n_{H,d} = 4.23 n_{C_3S} + 3.58 n_{C_2S} + 21.1 n_{C_3A} + 12.7 n_{C_4AF} + 1.97 n_{C\bar{S}}. \quad (42)$$

In Eq. (41), the mass fraction of $C\bar{S}$ appears; if the mass of gypsum ($C\bar{S}H_2$) had been used as the fit parameter, the appropriate coefficient would be 0.207 (Eq. (42) obviously would be unaltered). Note that the calcium sulphates react much faster than the other four clinker minerals, but that the formation of ultimate gypsum containing hydration products follows the hydration of the four major clinker phases, in particular, the C_3A (as we will see in [15]).

For each individual clinker phase, one can see that Eqs. (41) and (42) yield very similar values as provided by Eqs. (9) and (10), respectively, although the former fit is based on data for 39 cements and the latter on more than 100 cements. In Table 1, w_d/c computed via with Eq. (41) is also included. For all cements in Table 1, both Eq. (41) and the combination of Eqs. (32) and (32) and (36) (37) (38) provide values that are close to each other and are in good agreement with the experimental values. Eqs. (41) and (42) have as advantage that they provide the mass and moles of totally retained water as a function of each clinker phase, including calcium-sulphate. The mass and moles of gel water follow from subtracting Eq. (32) from Eq. (41) and Eq. (35) from Eq. (42), respectively:

$$w_g/c = 0.147 x_{C_3S} + 0.216 x_{C_2S} + 0.745 x_{C_3A} + 0.258 x_{C_4AF} + 0.261 x_{C\bar{S}}, \quad (43)$$

$$n_{H,g} = 1.86 n_{C_3S} + 2.07 n_{C_2S} + 11.1 n_{C_3A} + 6.96 n_{C_4AF} + 1.97 n_{C\bar{S}}. \quad (44)$$

For the saturated system, Eqs. (41)–(44) will be used henceforth.

3.3. Chemical shrinkage

To complete the model, the specific volumes of non-evaporable and gel water, v_n and v_g , which might both be compressed, also need to be specified. Both properties affect the shrinkage of the paste and possible uptake of water. Powers and Brownyard [1] measured the specific volume of saturated samples using a pycnometer method, with water as the displacement medium. In Appendix A, this work is summarised, and it is shown that the results are in agreement with later work on this topic by Copeland and Hayes [24] and Copeland [25].

The specific volume of nonevaporable water, v_n , was found to be $0.72 \text{ cm}^3/\text{g}$ and did not vary that much for all cements. Accordingly, one can use this value for assessing the specific volumes of all reaction products, including C-S-H (next section), the most abundant product. Furthermore, from the crystalline reaction products, the specific volumes at different water incorporations are known. This information confirms that $v_n = 0.72 \text{ cm}^3/\text{g}$ is a correct value for all hydration products [15].

The specific volume of the gel water and its possible compression (to $0.90 \text{ cm}^3/\text{g}$) has been subject of discussion [1,9,24,25], and up to now, the appropriate value of the effective specific volume is not decisively determined. But as we will see, for the crystalline reaction products, the specific volumes are known, and v_g can be determined, yielding $0.90 \text{ cm}^3/\text{g}$ [15]. In addition, also for the C-S-H, there are two indications that the adsorbed (gel) water is compressed to $0.90 \text{ cm}^3/\text{g}$.

First, Table 1 shows the chemical shrinkage of the cements using Eqs. (11), (32) and (36)–(38), computed with $v_n = 0.72 \text{ cm}^3/\text{g}$ and both with $v_g = 1$ (uncompressed) and $0.9 \text{ cm}^3/\text{g}$ (compressed). This shrinkage is expressed in mass of imbibed water per mass of hydrated cement. Obviously, when the gel water is also compressed, shrinkage is largest. This larger imbibition of CEM I paste was studied and measured in detail by Czernin [26] and Tazawa et al. [27]. The first author found $V_s/v_{wc} \approx 0.06$ after 28 days hydration, although its numerical value was still rising (hydration was far from completed); Tazawa et al. [27] measured $V_s/v_{wc} \approx 0.05$ after 28 days of hydration. Powers and Brownyard (Ref. [1], p. 266) mention a typical imbibition of 8.2 g water/100 g of reacted cement ($V_s/v_{wc} = 0.082$). From Table 1, it follows that when the gel water is compressed, these measured imbibitions are better matched. Note that the values of v_n and v_g do not depend on the content of clinker phases and seem to hold for all hydration products, although the shrinkage, as such, is obviously not the same for all cements. The reason is that the magnitude of shrinkage is also governed by w_n and w_g , which, in turn, are directly related to the clinker composition of cement (see Eqs. (32) and (37) or (43)).

Second, recently, molecular dynamics (MD) simulations have become available to model the sorption of water [28]. An important property in this regard is the energy of adsorption. Using B.E.T. theory for two cements (16186 and 16189, which are compatible with 15922 and 15756, respectively), Powers and Brownyard (Ref. [1], pp. 551–578) derived a value of 500 cal/g (Fig. 4), which is about 37.716 kJ/mol. As they expect this value to be an underestimation of 25–35%, MD simulations of sorption on a smooth surface with water adsorption energy of 50 kJ/mol have been executed [29], yielding a density profile that has a first maximum of 10 and a second maximum of 2.7. To interpret this in terms of density increases, one should average the density profile over a width comparable with the diameter of the water molecule. In the case of water, averaging the density over 3 Å by convoluting the density profile with a rectangular filter of that width reduces the variation of density. This results in an average density increase for water of 50% (at most) in the first layer and a 15% density increase in the second layer. Beyond that, there is no compression [29]. From these computations, one can derive that only water in the first and second layers is compressed (to 0.66 cm³/g and 0.85 cm³/g, respectively),

but water in the outer layers is uncompressed. Powers and Brownyard [1] derived that the maximum number of water layers at saturation is four, Hagymassy et al. [22] determined their maximum number to be five to six. Taking an average of five layers, the average specific volume of these five water layers can now be computed as 0.90 cm³/g.

Next, using $v_c = 0.32$ cm³/g, $v_w = 1$ cm³/g, $v_n = 0.72$ cm³/g and $v_g = 0.9$ cm³/g, the volume properties v_{hc} , v_{hp} (saturated), v_{hp} (P-dried) and Φ_g are computed in Table 1, using Eqs. (19)–(21), respectively. The fits by Powers and Brownyard [1] are used for computing these properties; had Eqs. (41) and (43) been used, practically the same values would have been obtained. The volume of the gel space (porosity of the hydration product Φ_g) is about 27–32%. The computed values are in accord with the values obtained by Powers and Brownyard [1], Powers [9,10] and Copeland [25].

Table 1 includes the theoretical ratios, w_d/c , for CEM I, computed with Eqs. (32), (36)–(38), and with Eq. (41). It follows that $w_d/c > 0.39$ is sufficient for complete hydration. Subsequent literature mentions that the “theory of Powers and Brownyard” requires $w_t/c_0 > 0.42$ – 0.44 for complete hydration [2,7,8,13], which is obviously not true for CEM I. This difference can be attributed to later publications of Powers [9,10], in which a cement with $w_d/c = 0.44$ is used as an example. This value originates from Cement 15754, which is of quite different composition than CEM I (Table 1). Powers and Brownyard [1] actually also mentioned $w_d/c = 0.40$ (p. 708), and from Fig. 3, even a value of 0.32. In this latter case, most probably, w_0/c_0 is meant, not including imbibed external water (about 7–8 g water/100 g cement) so that w_t/c_0 becomes 0.39.

3.4. Discussion

In later publications, the accuracy of the determination of chemically water bound water by P- and D-drying has been questioned [30,31]. These drying conditions are so severe, especially during D-drying, that also part of the chemically bound water is removed (dehydration), both from gel and crystalline reaction products (as was observed by Powers and Brownyard [1]). It should be noted that Feldman [31] heated the hydrated cement samples to 80 °C, subjected them to an extremely low pressure of 10⁻⁶ mm Hg and performed sorption experiments at the boiling temperature of nitrogen (–196 °C). These testing conditions are so severe that they are hardly comparable with the relatively milder P- (or even D-) drying experiments and the subsequent sorption experiments by Powers and Brownyard [1].

Furthermore, also the use of water as adsorption medium for measuring the B.E.T. surface (via V_m) was disputed. In fact Powers [9] admits that the measured V_m probably is not the theoretical correct one. Later nitrogen sorption gave values that are 1/5 to 1/3 of the value as determined with water [30,31], a finding also reported by Powers [9] and Brunauer and Greenberg [32]. Later, Hagymassy et al. [22] explained that, in contrast to water, nitrogen is unable to

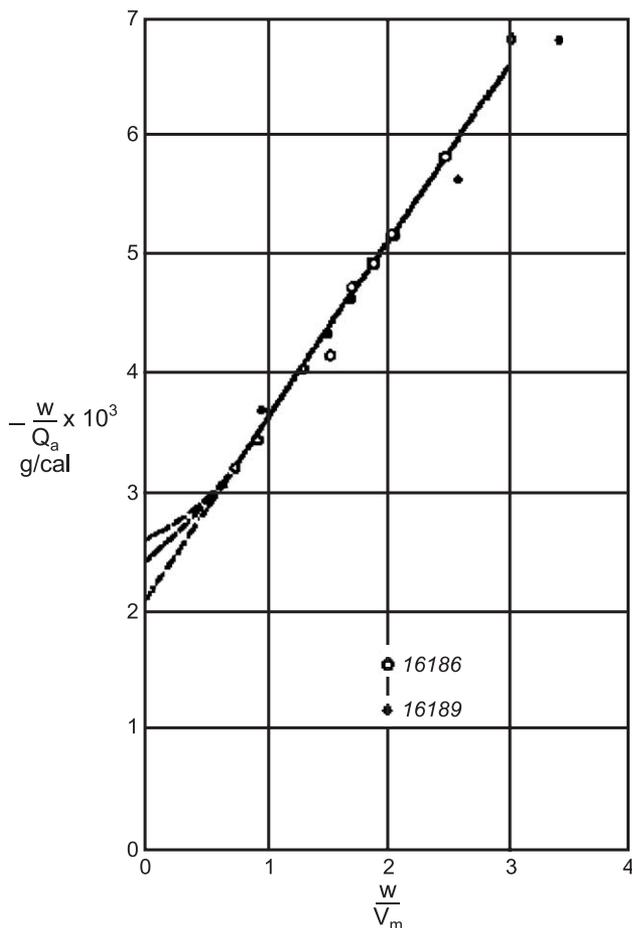


Fig. 4. Plot for evaluating constants of net heat of adsorption equation (Fig. 4.8, taken from p. 570, Ref. [1]).

enter all pores. For their pycnometer experiments, Powers and Brownyard (Ref. [1], pp. 692–694) also discussed critically various displacement media, being aware that some space might be inaccessible to inert gases and/or larger molecules.

For determining the total retained water, i.e., nonevaporable plus gel water, the methods of Powers and Brownyard [1] presented in this section are very useful. They are based on a large number of carefully executed experiments, whereby the combination of relatively mild P-drying and water as absorption medium provide valuable results, although it is very likely that part of the gel water is actually chemically bound (especially for the crystalline hydration products) while the other part is adsorbed (in the C-S-H). However, the total of nonevaporable plus gel water still comprises the total retained water. In this respect, the significant fact that gel water and nonevaporable water are directly related is also a remarkable and very useful result. Furthermore, the significance and magnitude of gel water (i.e., being $4V_m$) were independently confirmed by freezing/thaw experiments by Powers and Brownyard (Ref. [1], pp. 959–968).

The P-drying method and quantification of w_n/c is very useful to determine the degree of hydration. This is the reason why V_m and w_g can be related to w_n . It has also become clear that the concept of nonevaporable and gel water is useful for determining the chemical shrinkage of the system per mass of reacted cement, as is related to w_n/c and w_g/c . Furthermore, the model of Powers and Brownyard [1] makes a clear distinction, on one hand, between nonevaporable and gel water, and on the other, capillary pore water (see also Fig. 3). That the measured B.E.T. surface using water is approximate (at least) is not relevant for the amount of retained gel water either. The proportionality with the amount of gel water is already a useful result. The amount of gel water is relevant, and an alternative B.E.T. surface will only result in a modification of the number of absorbed layers; for example, it would be larger than four if this surface is reduced and vice versa.

Summarising, although the meaning of some measured chemical and physical properties might be disputed, the overall measured amounts of nonevaporable and gel water are very useful to obtain total retained water, gel porosity, and can be used to assess shrinkage and the prevailing chemical reactions of the individual clinker phases. To this end, the water retention in P-dried and saturated states will be used in the next section to study the hydration of the calcium silicate phases. In a forthcoming publication, the hydration reactions of the three other phases are examined [15]. Furthermore, the information on the specific volume of the compressed water will be used to quantify the porosity and density of the C-S-H. Note that the approach by Powers and Brownyard [1], also followed here, relates the water binding by hydration products formed from the reacted four (here, five) major clinker phases. These clinker phases comprise the major oxides C, S, A, F and \bar{S} . Implicitly, their approach prevents the remaining minor oxides (the

alkalis, MgO etc.) from combining with water. This implies that upon the reaction of the cement, these oxides enter the hydration product without mass increase. As x_{RO} is usually small (e.g., see Table 1), this approach is allowed.

4. Reactions of calcium silicate phases

Powers and Brownyard [1] presented a literature review of the reactions products and were aware that the products of the clinker phases C_3S and C_2S were “microcrystalline” CH and a “colloidal gel”, also named “colloidal hydrous silicate” and “calcium silicate hydrate” (pp. 106–132, 260 and 488). In later work, this product was called “tobermorite gel” [23,32–35], and nowadays, it is generally called C-S-H [2]. It is known to be a poorly crystalline to almost amorphous material.

Both calcium silicate phases and said reaction products are abundant in cement paste, and here, the reactions that take place in case other clinker phases are absent are discussed. By Brouwers [15], the reaction in combination with ferrite phase is addressed. Accordingly, here, the following relations are put forward:



Note that at that time x , the C/S ratio was unknown, although it was known that the C_2S reaction hardly produces CH (Ref. [1], p. 488). In other words, x should be close to 2, being in agreement with the present knowledge of x being in the range 1.5 to 2. The C/S ratio depends, among others, on the hydration conditions (bottle, paste), particle size, age and the analytical method employed [2].

Eq. (46) was proposed by Locher [12], who was the first to couple the overall nonevaporable water of Portland cement (thus, not C_3S in particular), as determined by the method by Powers and Brownyard [1], to the hydration of C_3S .

Note that $(2 - x + y)$ and $(3 - x + y)$ correspond to n_H , and that $n_{C_2S} = 1$ and $n_{C_3S} = 1$ in Eqs. (45) and (46), respectively. The value of n_H depends on the drying conditions (see Eqs. (35) and (42) for their values in P-dried and saturated states, respectively).

4.1. P-dried state

Based on the findings of Brunauer and Greenberg [32], Brunauer et al. [33] and Kantro et al. [35], P-drying only removes water from the C-S-H but not from CH, and it does not affect the C/S (x) ratio of the C-S-H.

X-ray analysis on P-dried C_2S and C_3S /alite by Kantro et al. [35] revealed that $(x - y)$ amounts to 0.5 and 0.4 in C-S-H formed by C_2S and C_3S /alite, respectively. These values are stable up to 1700 days for water–cement ratios ranging from 0.45 to 0.7. From Eq. (35), it follows $n_{C_2S} = 1$ and $n_{H,n} = 1.51$ for the C_2S reaction, thus, $(x - y)$ equals 0.49.

Table 4a
Properties C₃S and C₂S and their hydration products (C-S-H+CH)

Clinker mineral	v_c (cm ³ /g)	ρ_{hc} (g/cm ³)	v_d (cm ³ /g)	ρ_{hp} (P-dried) (g/cm ³)	ρ_{hp} (saturated) (g/cm ³)	Φ_g	V_s/vw_c
C ₃ S ^a	0.321	2.61	0.80	2.02	2.27	23%	6.7%
C ₂ S ^a	0.301	2.79	0.82	1.90	2.26	32%	6.6%
C ₃ S ^b	0.321	2.61	0.84	1.97	2.22	24%	5.2%
C ₂ S ^b	0.301	2.79	0.88	1.84	2.18	34%	4.4%

The properties are computed using the values of w_n/c , w_g/c and w_d/c as given by Eqs. (32), (43) and (41), respectively, with $x_{c_3s}=1$ and $x_{c_2s}=1$ substituted.

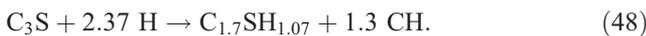
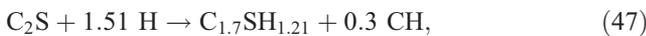
^a v_c is taken from Table 1, $v_n=0.72$ cm³/g, and $v_g=0.9$ cm³/g.

^b v_c is taken from Table 1, $v_n=0.72$ cm³/g, and $v_g=1$ cm³/g.

For the C₃S/alite reaction, $n_{C_3s}=1$ and $n_{H,n}=2.37$, hence, $(x-y)=0.63$. For C₂S, the agreement with the aforesaid values of Kantro et al. [35] is excellent, for C₃S/alite, it is very good. Note that Locher [12] experimentally found $n_{H,n}=2.66$, i.e., the coefficient of C₃S in Eq. (32) being 0.21 instead of 0.187. This value corresponds to $(x-y)=0.34$; this figure is in better agreement with the aforementioned value in Kantro et al. [35].

The specific volume (density) of the hydrated cement follows from Eq. (19), in which v_c , ($=1/\rho_c$, see Table 2 for the values of C₂S and C₃S), $v_n=0.72$ cm³/g and w_n/c (Eq. (32)) have been substituted; the resulting ρ_{hc} is included in Table 4a ($\rho_{hc}=1/v_{hc}$). For the C₃S reaction, $x_{C_3s}=1$ in Eq. (32), while for the C₂S reaction, $x_{C_2s}=1$ in Eq. (32). Thus, the P-dried hydrated C₃S has a lower density than C₂S does because the reaction product of C₃S contains relatively more CH, which has a lower density than the intrinsic density of C-S-H, as will follow below.

This density (reciprocal of the specific volume) of P-dried C-S-H is an interesting property. To determine the quantities of the two reaction products formed, the C/S ratio, x in Eqs. (45) and (46), needs to be specified. An average value of 1.7 is often found and is generally accepted [2,12,13,20,32,33]. This value yields the following approximate reactions



The resulting molecular mass of C-S-H is included in Table 4b. The density of the hydrated cement, which is

composed of C-S-H and CH (the right-hand sides of Eqs. (47) and (48)), reads:

$$\rho_{hc} = y_{C-S-H} \rho_{C-S-H} + y_{CH} \rho_{CH}. \quad (49)$$

In Eq. (49), y_{C-S-H} and y_{CH} represent the volume fractions of C-S-H and CH in the hydrated cement, respectively, whereby $y_{C-S-H} + y_{CH} = 1$. Both ρ_{CH} (Table 2) and ρ_{hc} (Table 4a), appearing in Eq. (49), are known.

Rewriting Eq. (49) yields

$$\rho_{C-S-H} = \frac{\rho_{hc} - y_{CH}\rho_{CH}}{1 - y_{CH}}. \quad (50)$$

The volume fraction is related to the mass fraction by

$$y_{CH} = \frac{x_{CH}\rho_{hc}}{\rho_{CH}}. \quad (51)$$

The mass fraction of CH in the hydrated C₂S clinker can be derived from Eq. (45) and reads

$$x_{CH} = \frac{(2-x)M_{CH}}{M_{C_2s} + (2-x+y)M_H}. \quad (52)$$

Substituting M_{CH} , M_H , M_{C_2s} (Table 2) and $2-x+y=1.51$ (see Eq. (47)), yields x_{CH} and x_{C-S-H} (Table 4b). With ρ_{hc} (Table 4a) and ρ_{CH} (Table 2), Eq. (51) yields y_{CH} and y_{C-S-H} , and Eq. (50), the intrinsic C-S-H density: $\rho_{C-S-H}=2.88$ g/cm³ (included in Table 4b). One can see that y_{C-S-H} is indeed smaller than x_{C-S-H} is, for the density of (P-dried) C-S-H is greater than that of CH (Tables 2 and 4b). Similarly, ρ_{C-S-H} from the C₃S reaction can be calculated using Eqs. (50)–(52), whereby in the latter $(2-x)$ is replaced by $(3-x)$, M_{C_2s} by M_{C_3s} and $(2-x+y=1.51)$ by $(3-x+y=2.37)$. This results in $\rho_{C-S-H}=2.87$ g/cm³; this value is included in Table 4b as well.

All computed values for ρ_{C-S-H} are in the same range of values reported by Brunauer and Greenberg [32] and Brunauer et al. [33] for the intrinsic C-S-H density, as well as with Feldman's [36], who measured $\rho_{C-S-H}=2.74$ g/cm³ for C-S-H produced by paste-hydrated C₃S (for bottle hydrated C₃S, on the other hand, $\rho_{C-S-H}=2.38$ g/cm³). Using the computed densities and molecular mass, one can also compute the molar specific volume of C-S-H (ω_{C-S-H} ; Table 4b).

Note that this latter value can also be obtained in an alternative way: The total molar volume of the right-hand

Table 4b
Properties of C-S-H formed from C₃S and C₂S hydration reactions, based on data from Table 4a

Source (state)	Composition C-S-H	M_{C-S-H} (g/mol)	ρ_{C-S-H} (g/cm ³)	ω_{C-S-H} (cm ³ /mol)	x_{C-S-H}	y_{C-S-H}	ϕ_{C-S-H}
C ₃ S (P-dried)	C _{1.7} SH _{1.07}	174.70	2.87	60.96	0.64	0.59	–
C ₂ S (P-dried)	C _{1.7} SH _{1.21}	177.24	2.88	61.47	0.89	0.86	–
C ₃ S (saturated) ^a	C _{1.7} SH _{2.93}	208.26	2.28	91.17	0.68	0.68	33%
C ₂ S (saturated) ^a	C _{1.7} SH _{3.28}	214.44	2.26	94.95	0.91	0.91	35%
C ₃ S (saturated) ^b	C _{1.7} SH _{2.93}	208.26	2.20	94.52	0.68	0.69	36%
C ₂ S (saturated) ^b	C _{1.7} SH _{3.28}	214.44	2.17	98.67	0.91	0.91	38%

^a For saturated C-S-H is used: $v_g=0.9$ cm³/g.

^b For saturated C-S-H is used: $v_g=1$ cm³/g.

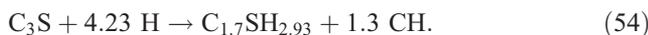
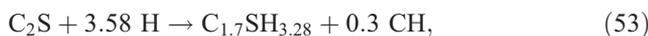
side of Eq. (47) is equal to the molar volume of the left-hand side, whereby the reacting water is compressed, thus being $0.72 \times 18.02 \text{ cm}^3/\text{mol} = 12.97 \text{ cm}^3/\text{mol}$ ($\omega_{\text{H,n}}$). Deducting the volume equivalent to 0.3 mol of CH then yields the same molar volume of C-S-H, as listed in Table 4b. The same procedure can be carried out with Eq. (48). Knowing the molar volume and molar mass, the density of C-S-H could subsequently be computed.

Alternative computations with $x=1.6$ and 1.8 result in $\rho_{\text{C-S-H}} = 2.90/2.92$ ($\text{C}_3\text{S}/\text{C}_2\text{S}$) and $2.83/2.85 \text{ g/cm}^3$ ($\text{C}_3\text{S}/\text{C}_2\text{S}$), respectively. These values are almost the same as the values found for $x=1.7$; thus, the obtained intrinsic density of P-dried C-S-H is not sensitive to the chosen C/S ratio.

Summarising, the foregoing analysis of the P-dried hydration products of C_3S and C_2S and the consistent conclusions support the values of w_n/c for C_3S and C_2S as given by Eq. (32) and the validity of specific volume of the nonevaporable water ($0.72 \text{ cm}^3/\text{g}$) for hydrated C_3S and C_2S .

4.2. Saturated state

The next step is to study the hydration of C_2S and C_3S in saturated conditions. From Eq. (41), it follows that $(2-x+y=3.58)$ and $(3-x-y=4.23)$ for the C_2S and C_3S reactions, respectively. Again, invoking $x=1.7$, Eqs. (45) and (46) yield the following reactions with approximate coefficients



Employing Eqs. (20) and (21), the specific volumes of the hydration products of C_2S and C_3S (CH and C-S-H) can be computed, both in saturated and in P-dried states, the reciprocals being included in Table 4a. The required w_n/c and w_g/c from both clinker phases are taken from Eqs. (32) and (43), respectively, whereby $x_{\text{C}_3\text{S}} = 1$ for the C_3S reaction and $x_{\text{C}_2\text{S}} = 1$ for the C_2S reaction. The specific volumes of both clinker phases are taken from Table 2. Results are given both for compressed and uncompressed gel water. The mean specific compressed water density, v_d , is computed with Eq. (4) and included in Table 4a as well.

The densities of the saturated hydration product (ρ_{hp} ranges from 2.18 to 2.27 g/cm^3 , Table 4a) are in good agreement with the value found by Hansen (quoted by Taylor [2]): 2.18 g/cm^3 . The porosity of the hydration products (comprising C-S-H and CH), Φ_g , is computed with Eq. (22) and is also included in Table 4a. From Table 4a, it follows that v_d is smaller when the gel water is compressed, and that also the gel porosity is smaller in case of compressed gel water.

In the literature, the densities of the hydration product corrected for CH can be found, i.e., the density of saturated C-S-H. For the C_2S reaction, this density can be computed with Eqs. (50)–(52), whereby ρ_{hc} is replaced by ρ_{hp}

(saturated, Table 4a) and $(2-x+y)=3.58$ instead of 1.51. Again, $x=1.7$, and M_{CH} , ρ_{CH} and $M_{\text{C}_2\text{S}}$ are taken from Table 2. This procedure yields ρ_{hp} (saturated) = $2.26/2.17 \text{ g/cm}^3$ (for $v_g=0.9/1 \text{ cm}^3/\text{g}$) for the saturated C-S-H density (Table 4b). Repeating the computation for the C_3S reaction yields $2.28/2.20 \text{ g/cm}^3$ (Table 4b). Hence, it follows that the densities of the saturated C-S-H, CH and the saturated hydration product (a mix of C-S-H and CH) do not differ much. The computed values of $x_{\text{C-S-H}}$ and $\rho_{\text{C-S-H}}$ in the saturated state are summarised in Table 4b. As the densities of saturated C-S-H and CH are comparable, the volume (y) and mass (x) fractions are also comparable (Table 4b).

A glance at Table 4a reveals that the porosity Φ_g of the hydration product (gel space) produced by the C_2S reaction (32–34%) is larger than for the C_3S reaction (23–24%). This would be expected, as this reaction relatively forms more C-S-H (compare Eq. (48) with Eq. (47)), and this saturated C-S-H is holding the gel water of the entire hydration product. As the C-S-H is much more porous than the crystalline CH (porosity almost zero) is, C-S-H porosities can be determined from the overall porosities Φ_g listed in Table 4a. Assuming the porosity of CH to be negligible, i.e., assigning the gel space completely to the C-S-H phase, it follows that

$$\Phi_g = y_{\text{C-S-H}} \Phi_{\text{C-S-H}}, \quad (55)$$

giving $\Phi_{\text{C-S-H}} = 35/38\%$ ($v_g=0.9/1 \text{ cm}^3/\text{g}$). Similarly, $\Phi_{\text{C-S-H}}$ can be computed from the C_3S reaction, giving $\Phi_{\text{C-S-H}} = 33/36\%$ (included in Table 4b). Computations with $x=1.6$ and 1.8 result in values that are very close to those aforesaid; thus, the obtained result is not very sensitive to the chosen C/S ratio. Furthermore, both C_2S and C_3S seem to produce C-S-H having a similar porosity with a typical value of 34% (assuming compressed gel water) or 37% (uncompressed gel water). This (gel) space will actually will be filled with 2.06 mol of water ($=3.58-1.51$, i.e., total water minus nonevaporable water) per mole of C-S-H (from C_2S) or 1.86 mol of water ($=4.23-2.37$) per mole of C-S-H (from C_3S) when the P-dried hydration product (more particularly, the C-S-H part of it) is saturated with water.

The computations with uncompressed gel water reveal, as expected, that the gel porosity of the C-S-H increases to the same extent (10%) as the specific volume of the water is increased (Table 4b). Data from the previous section suggests that $v_g=0.9 \text{ cm}^3/\text{g}$ is most likely; thus, the values in Tables 4a and 4b, based on the compressed gel water, seem to be preferred. The mass of imbibed water, $V_s/v_{\text{w,c}}$, also included in Table 4a, is in accord with previously reported values [26,27] when gel water is compressed. As C_2S and C_3S are the major clinker phases and C-S-H and CH the most abundant reaction products, the water imbibition again supports a value of $v_g=0.9 \text{ cm}^3/\text{g}$ for the gel water in C-S-H.

Furthermore, note that the molar specific volumes of C-S-H could also have been obtained with the total specific

volumes of the right-hand sides of Eqs. (53) and (54), deducted with the volumes by the CH, and taking account that part of the water is compressed to $12.97 \text{ cm}^3/\text{mol}$ (nonevaporable water) and the gel water part to $0.9 \times 18.02 \text{ cm}^3/\text{mol} = 16.22 \text{ cm}^3/\text{mol}$ ($\omega_{H,g}$).

The H/S values for saturated C-S-H found here are lower than the H/S ratio put forward by Young and Hansen [13]. These authors studied the reaction of pure and fully hydrated C_3S and proposed $C/S = 1.7$ and $H/S = 4$ for the C-S-H thus formed. This water content was based on dynamic shrinkage–weight loss curves of thin specimens of C_3S paste; whereby the time allowed for hydration was not specified. From Lu et al. [37], it follows that the H/S ratio decreases with hydration time: $H/S = 4.56$ (3 days), 3.93 (28 days) and 3.60 (60 days). The H/S value after 126–479 days of curing derived here, namely, $H/S = 3.2$, is compatible with this trend. In other words, water-saturated C-S-H binds an excess of water at early ages (supersaturation), which is released.

Based on the aforementioned high H/S, Young and Hansen [13] found by extrapolation that the density of C-S-H should range from 1.85 to 1.90 g/cm^3 in the saturated state. The authors compared this with the saturated gel density of 1.76 g/cm^3 “as computed by Powers [10]”. But Powers [10] actually mentions that the “dry weight of cement gel” (i.e., dried hydration product) attains a value of $0.567 \text{ cm}^3/\text{g}$ ($= 1.76 \text{ g/cm}^3$), hence, not referring to the saturated gel (hydration product) but, rather, to the dried gel, i.e., ρ_{hp} (P-dried).

On the other hand, the H/S ratio for saturated C-S-H found here are in accord with the values found by Fujii and Kondo [38,39] and Taylor [40]. Based on synthesized C-S-H gels from a solution, the former authors found the composition $C_xSH_{x+0.8}$ and, later, $C_xSH_{x+0.92}$. The authors considered C-S-H to be a solid solution of CH and a calcium silicate hydrate. Based on an experimental analysis of mature cement pastes, Taylor [40] derived a similar formulation for saturated C-S-H: $C_xSH_{x+1.7}$. Substituting $x = 1.7$ into these formulations yields compositions that are close to $C_{1.7}SH_{3.2}$ found here.

Based on the previous section and in the foregoing discussion on the hydration of alite and belite, here, it is concluded that for cement (and C-S-H), the density of saturated hydration product ρ_{hp} (saturated) is typically 2.25 g/cm^3 .

4.3. Properties C-S-H

To facilitate the modeling of cement hydration reactions, it is desirable to define a composition, molar volume and density of (mature) P-dried and saturated C-S-H that can be used for the C_3S and C_2S reactions. On the basis of the present results, a representative overall formulation of P-dried C-S-H would comprise $C_{1.7}SH_{1.2}$, with a density of 2.86 g/cm^3 (Table 2). This density is based on the specific molar volumes that follow from the present analysis of the C_3S and C_2S reactions, whereby the difference in non-

evaporable water content is accounted for by using $12.97 \text{ cm}^3/\text{mol}$ as the effective molar volume of the combined water. On the basis of the values listed in Table 4b, in the case of compressed gel water ($\omega_{H,g} = 16.22 \text{ cm}^3/\text{mol}$), it follows that $C_{1.7}SH_{3.2}$ ($M_{C-S-H} = 213.1 \text{ g/mol}$) and $\omega_{C-S-H} = 94.6 \text{ cm}^3/\text{mol}$ (i.e., $\rho_{C-S-H} = 2.25 \text{ g/cm}^3$ and $\Phi_{C-S-H} = 34\%$) provides the best results. The proposed compositions of the C-S-H and its properties are included in Table 2. This molar volume is based on the specific molar volumes of C-S-H that follow from the present analysis of the C_3S and C_2S reactions (Table 4b), whereby the difference in gel water content is accounted for by using $16.22 \text{ cm}^3/\text{mol}$ as molar volume of this water.

For the computation of the molar volume of saturated C-S-H that has higher water content (e.g., young paste), from the previous section, it follows that the additional water (layers) will not be compressed and should be assigned a specific molar volume of $18.02 \text{ cm}^3/\text{mol}$ (as most likely only the first two water layers are compressed). Hence, the density and porosity can be expressed as follows

$$\rho_{C_{1.7}SH_{3.2+y}} = \frac{213.09 + 18.02y}{94.60 + 18.02y} \left[\frac{\text{g}}{\text{cm}^3} \right], \quad (56)$$

$$\Phi_{C_{1.7}SH_{3.2+y}} = \frac{32.44 + 18.02y}{94.60 + 18.02y}, \quad (57)$$

respectively, with $y \geq 0$. For $y = 0$, Eqs. (56) and (57) yield the values included in Table 2. When $y = 0.8$ is substituted, $\rho_{C-S-H} = 2.0 \text{ g/cm}^3$, which comes closer to the values reported in [13], namely 1.85 – 1.90 g/cm^3 , as discussed above. From Lu et al. [37], it follows that the H/S ratio decreases with hydration time: $H/S = 4.56$ (3 days), 3.93 (28 days) and 3.60 (60 days), implying $y = 1.36$ (3 days), 0.73 (28 days) and 0.40 (60 days) if the paste is supersaturated, while from this study, it follows that $y = 0$ for saturated mature paste (aged for half a year or so and longer). A function of the form $H/S = 3.2 + y = 3.2 + g_1 \exp(-g_2 t)$ is fitted through the data of Lu et al. [37], yielding $g_1 = 4.60$ and $g_2 = -2.23 \times 10^{-2} \text{ day}^{-1}$. In Fig. 5, the data and fit are depicted.

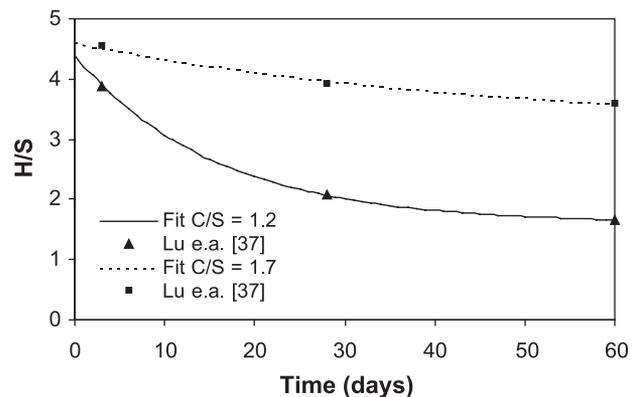


Fig. 5. Experimental data by Lu et al. [37] and fits.

When the relative humidity drops below 100%, $-2 \leq y < 0$ applies. The value of y versus the relative humidity is assessed with the cement gel isotherm (Fig. 2) given by Powers and Brownard [1] and assuming that this isotherm is applicable to pure C-S-H, being the most abundant reaction product. The said gel isotherm relates w_g/V_m to the relative humidity, and at relative humidities of approximately 0% (P-dried) and 100%, indeed, w_g/V_m amounts to 0 and 4, respectively (see Section 3), which will correspond to 0 ($y = -2$) and 2 ($y = 0$) mol of gel water retained, respectively. For relative humidities of 11%, 40% and 80%, w_g/V_m amounts to 0.8, 1.5 and 2.5, respectively, corresponding to $C_{1.7}SH_{1.6}$ ($y = -1.6$), $C_{1.7}SH_2$ ($y = -1.2$) and $C_{1.7}SH_{2.5}$ ($y = -0.7$), respectively. The composition at 11% RH is in accord with the values reported by Taylor [2], and the water content is lower (again) than found by Young and Hansen [13] ($C_{1.7}SH_{2.1}$). This difference might be caused by the age of their paste, as discussed in the foregoing. For $-2 \leq y < 0$, the gel space is not completely filled with water anymore. Based on this concept, the gel space still amounts $2 \times 16.22 \text{ cm}^3/\text{mol}$ ($= 32.44 \text{ cm}^3/\text{mol}$) per mole of C-S-H, for all RHs. For all relative humidities, the porosity thus follows from Eq. (57), with $y = 0$ substituted, being the previously mentioned 34%.

In the range $-2 \leq y < 0$, the gel space is not completely filled with water anymore, while the total volume of the C-S-H remains constant. The density in this range therefore reads

$$\rho_{C_{1.7}SH_{3.2+y}} = \frac{213.09 + 18.02y}{94.60} \left[\frac{\text{g}}{\text{cm}^3} \right], \quad (58)$$

In the foregoing, some physical properties of C-S-H have been specified for $C/S = 1.7$, (super-)saturated at different ages and unsaturated (when the RH drops below 100%). Based on the information from the present study, it is also possible to assess the properties for $C/S \neq 1.7$.

As first step, the composition in the P-dried state is considered. As discussed before, in this section, Kantro et al. [35] and Taylor [40] found formulations of the type C_xSH_{x+y} , applicable to $1 \leq x \leq 2$, whereby y amounts to -0.5 and -0.25 , respectively. Lu et al. [37] found $x = 1.2$ and $y = -0.70$ after 60 days. Accordingly, the formulation $C_xSH_{x-0.5}$ seems appropriate to P-dried C-S-H, implying that C and H are reduced to the same extent. This is compatible with Fujii and Kondo [38,39], who modelled C-S-H as a solid solution of CH and a calcium silicate hydrate. Accordingly, a change in the C/S ratio (x) of the C-S-H is modelled by a change in CH content; using the molar masses and volumes of $C_{1.7}SH_{1.2}$ and CH (Table 2), the following expression is put forward for P-dried C-S-H in case $C/S \neq 1.7$:

$$\begin{aligned} \rho_{C_xSH_{x-0.5}} &= \frac{177.05 + 74.10(x - 1.7)}{62 + 33.05(x - 1.7)} \left[\frac{\text{g}}{\text{cm}^3} \right] \\ &= \frac{51.08 + 74.10x}{5.82 + 33.05x} \left[\frac{\text{g}}{\text{cm}^3} \right], \end{aligned} \quad (59)$$

The next step is to determine the composition and physical properties of saturated C-S-H. From the literature, one cannot conclude unambiguously the amount of evaporable water for $C/S \neq 1.7$. Accordingly, two concepts are discussed.

Case 1: constant gel water

Fujii and Kondo [38,39] and Taylor [40] found formulations of the type C_xSH_{x+y} for saturated C-S-H, likewise for P-dried C-S-H, whereby now, $y = 0.8 - 1.7$. Taylor [40] gives $y = 1.7$ for saturated C-S-H and $y = -0.25$ for P-dried C-S-H, implying that an extra 1.95 mol of water are retained when 1 mol of P-dried C-S-H is saturated, regardless of the value of x . For $x = 1.7$, this H/S value of 1.95 is compatible with the H/S value of 2 found here. Based on the foregoing literature, a change in the C/S ratio (x) of the C-S-H is modelled by a change in CH content, whereas the amount of gel water remains unchanged. Using the molar masses and volumes of $C_{1.7}SH_{3.2}$ and CH (Table 2), the following expression is put forward for saturated C-S-H, $C/S \neq 1.7$ and $-2 \leq y < 0$ as:

$$\begin{aligned} \rho_{C_xSH_{x+1.5+y}} &= \frac{213.09 + 74.10(x - 1.7) + 18.02y}{94.60 + 33.05(x - 1.7)} \left[\frac{\text{g}}{\text{cm}^3} \right] \\ &= \frac{87.12 + 74.10x + 18.02y}{38.42 + 33.05x} \left[\frac{\text{g}}{\text{cm}^3} \right], \end{aligned} \quad (60)$$

See also Eq. (58), which holds for mature paste. For $-2 \leq y < 0$, the gel space is not completely filled with water anymore, but its volume is not affected.

Based on the present C-S-H model, the gel space amounts to $2 \times 16.22 \text{ cm}^3/\text{mol}$ ($= 32.44 \text{ cm}^3/\text{mol}$) per mole of C-S-H, for all C/S and for $-2 \leq y < 0$ (all RH); therefore, the porosity follows as

$$\Phi_{C_xSH_{x+1.5}} = \frac{32.44}{94.60 + 33.05(x - 1.7)}, \quad (61)$$

According to this equation, the gel porosity increases with smaller C/S (x) as the gel water remains 2 mol of water/mol of C-S-H, whereas the P-dried mass decreases.

As said, the present C-S-H model is based on the concept of 2 H/S gel water for all C/S ratios at RH = 100%. To determine y versus other RH, one could use the information provided by the gel isotherm for $C/S = 1.7$, again, yielding the general expressions $C_xSH_{x-0.1}$ ($y = -1.6$), $C_xSH_{x+0.3}$ ($y = -1.2$) and $C_xSH_{x+0.8}$ ($y = -0.7$) for RH of 11%, 40% and 80%, respectively, applicable to all C/S.

Case 2: variable gel water

Lu et al. [37] found that the amount of gel water is lower when C/S drops from 1.7 to 1.2. In addition, for $C/S = 1.2$, they measured a decreasing H/S ratio with hydration time: H/S = 3.89 (3 days), 2.07 (28 days) and 1.66 (60

days), implying that saturated mature C-S-H tends to formulation $C_{1.2}SH_{1.6}$. A function of the form $H/S = 1.6 + y = 1.6 + g_1 \exp(-g_2 t)$ is fitted through the data of Lu et al. [37], yielding $g_1 = 4.39$ and $g_2 = -6.39 \times 10^{-2} \text{ day}^{-1}$. In Fig. 5, the data and fit are included. The lower value of g_2 and the figure indicate that the pozzolanic C-S-H tends swifter to its ultimate value than the OPC C-S-H does ($C/S = 1.7$). The formulation found by Lu et al. [37] also indicates that the gel water amounts to about 1 H/S when $C/S = 1.2$, and not 2 H/S. A reduction of the C/S ratio with 0.5 seems to reduce the gel water with 1 H/S. The quantity of gel water is therefore modelled as $H/S = (2x - 1.4)$ instead of $H/S = 2$. Subsequently, the following alternative formulations for the density and porosity of C-S-H are derived:

$$\begin{aligned} \rho_{C_xSH_{3x-1.9+y}} &= \frac{213.09 + 74.10(x - 1.7) + 18.02(y + 2x - 3.4)}{94.60 + 33.05(x - 1.7) + 16.22(2x - 3.4) + 18.02y} \\ &\quad \times \left[\frac{\text{g}}{\text{cm}^3} \right] \\ &= \frac{25.85 + 110.14x + 18.02y}{-16.73 + 65.49x + 18.02y} \left[\frac{\text{g}}{\text{cm}^3} \right], \end{aligned} \quad (62)$$

$$\begin{aligned} \Phi_{C_xSH_{3x-1.9+y}} &= \frac{32.44 + 16.22(2x - 3.4) + 18.02y}{94.60 + 33.05(x - 1.7) + 16.22(2x - 3.4) + 18.02y} \\ &= \frac{-22.71 + 32.44x + 18.02y}{-16.73 + 65.49x + 18.02y} \left[\frac{\text{g}}{\text{cm}^3} \right], \end{aligned} \quad (63)$$

with $y \geq 0$. For $C/S = 1.7$, Eqs. (62) and (63) yield Eqs. (56) and (57), respectively. The variable amount of gel water (gel space) is accounted for by $16.22 \text{ cm}^3/\text{mol}$. On the other hand, for young and supersaturated paste ($y \geq 0$), the additional water (layers) are not compressed and are assigned a specific molar volume of $18.02 \text{ cm}^3/\text{mol}$ in Eqs. (62) and (63). Fig. 5 shows the value of y versus age for $C/S = 1.2$ and 1.7 .

For unsaturated C-S-H holds $-(2x - 1.4) \leq y < 0$. Using the molar masses and volumes of $C_{1.7}SH_{3.2}$ and CH (Table 2), the following expression is put forward for saturated C-S-H, $C/S \neq 1.7$ and $-(2x - 1.4) \leq y < 0$:

$$\begin{aligned} \rho_{C_xSH_{3x-1.9+y}} &= \frac{213.09 + (x - 1.7)74.10 + 18.02(y + 2x - 3.4)}{94.60 + (x - 1.7)33.05 + (2x - 3.4)16.22} \left[\frac{\text{g}}{\text{cm}^3} \right] \\ &= \frac{25.85 + 110.14x + 18.02y}{-16.73 + 65.49x} \left[\frac{\text{g}}{\text{cm}^3} \right], \end{aligned} \quad (64)$$

See also Eq. (58), which holds for mature paste. For $-(2x - 1.4) \leq y < 0$, the gel space is not completely filled

with water anymore. For all C/S and for $-(2x - 1.4) \leq y < 0$ (all relative humidities), therefore, the porosity follows as

$$\begin{aligned} \Phi_{C_xSH_{3x-1.9+y}} &= \frac{32.44 + 16.22(2x - 3.4)}{94.60 + 33.05(x - 1.7) + 16.22(2x - 3.4)} \\ &= \frac{-22.71 + 32.44x}{-16.73 + 65.49x}. \end{aligned} \quad (65)$$

In contrast to Eq. (61), upon reducing C/S, the gel volume of mature C-S-H is also reduced.

In Fig. 6a, the C-S-H volumes according to Eqs. (61) and (65) are depicted versus C/S. In Fig. 6b, the densities of saturated ($y = 0$) C-S-H according to Eqs. (60) and (62) are depicted versus C/S. One can see that both models yield $\Phi_{C-S-H} = 34\%$ and $\rho_{C-S-H} = 2.25 \text{ g/cm}^3$ at $C/S = 1.7$, as expected. But for $C/S \neq 1.7$, the two cases predict an opposite trend; Case 1 reflects a decreasing porosity with larger C/S, while Case 2 reflects an increasing porosity for larger C/S. Furthermore, Case 1 implies an almost constant saturated

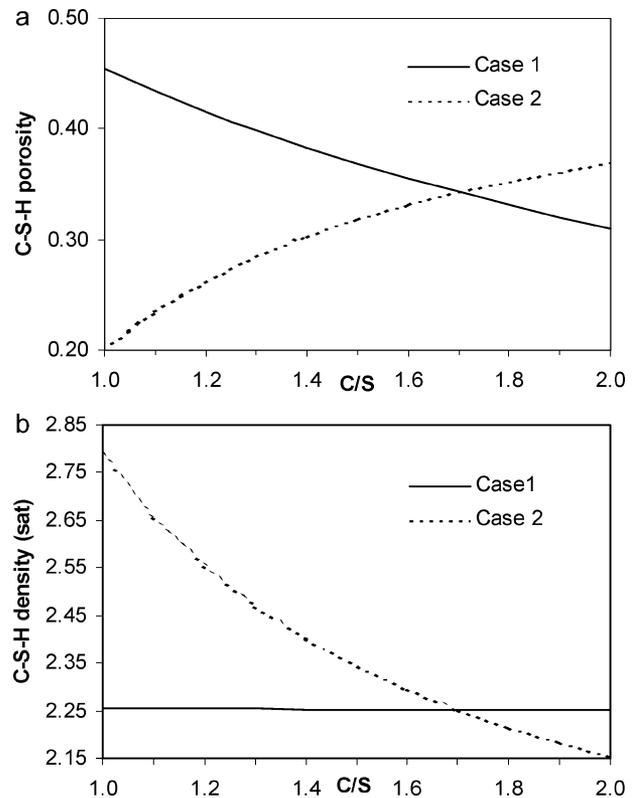


Fig. 6. (a) C-S-H gel porosity vs. the C/S for Case 1 (gel water is constant: 2 H/S) and Case 2 (gel water depends on C/S ratio). (b) Saturated C-S-H density in g/cm^3 vs. the C/S for Case 1 (gel water is constant: 2 H/S) and Case 2 (gel water depends on C/S ratio).

C-S-H density, whereas Case 2 reflects an decreasing density for increasing C/S.

5. Conclusions

Powers and Brownyard [1] presented a model that accounts for unreacted cement, free water, the hydration product (which is porous in itself, i.e., gel porosity) and chemical shrinkage (Fig. 1). Careful execution of experiments resulted in quantity and specific volume of both nonevaporable water and gel water. The water retention in P-dried and saturated states was further-related to the mineralogical composition of the cement.

The most important features of the model are discussed in detail in this paper, and applied to the individual reactions of the two major clinker phases: alite and belite (aluminates and ferrite are addressed later: Ref. [15]). This application, making use of water retention in P-dried and saturated states, gives quantitative information on the hydration products formed (after 126 days and longer), namely, $C_{1.7}SH_{3.2}$ and CH. P-dried C-S-H appears to have a formulation $C_{1.7}SH_{1.2}$, and upon saturation, 2 H/S (gel water) extra are retained. The density (2.25 g/cm^3) and porosity (34%) of C-S-H are derived for $C/S=1.7$. In case the first layer or first two layers (which are compressed) are excluded from this gel porosity, it will amount to 29% or 23%, respectively. Furthermore, an assessment is made for the magnitude of these properties in case $C/S \neq 1.7$. For this latter situation, two cases (assumptions) are distinguished, based on the amount of gel water retained (Fig. 6a and b).

To determine the aforesaid properties, two important properties of the model of Powers and Brownyard [1], viz the specific volume of nonevaporable water (v_n) and of gel water (v_g) are used. Hitherto, particularly the latter value and the question of gel water being (un-)compressed was subject of discussion, which was not yet finally decided. From the reaction equations and products, it follows that $v_g=0.90 \text{ cm}^3/\text{g}$ is most appropriate (compressed).

Summarizing, the present analysis not only clarifies the model and experiments by Powers and Brownyard [1], but based on their work, also derives some major properties of the calcium silicate reactions and their reaction products.

6. List of symbols

Roman

<i>A</i>	Al_2O_3
<i>B</i>	$=B' + 1 = (w_g + w_n)/w_n$
<i>B'</i>	w_g/w_n
<i>c</i>	Mass of reacted cement [g]

c_0	Initial mass of unreacted cement [g]
<i>C</i>	CaO
C_3A	Aluminate or pure C_3A
CH	Portlandite
C_3S	Alite or pure C_3S
C_2S	Belite or pure C_2S
C-S-H	Calcium silicate hydrate
$C\bar{S}$	Anhydrite
$C\bar{S}H_{0.5}$	Hemihydrate
$C\bar{S}H_2$	Gypsum
C_4AF	Ferrite or pure C_4AF
<i>F</i>	Fe_2O_3
<i>H</i>	H_2O
<i>k</i>	Number of absorbed layers of gel water
<i>M</i>	Mass of 1 mol of substance [g/mol]
<i>m</i>	Mass of reacted phase or formed product [g]
<i>m</i>	Maturity factor (degree of hydration), c/c_0
<i>n</i>	Number of moles
RH	Relative humidity
RO	Remaining oxides in clinker
<i>S</i>	SiO_2
\bar{S}	SO_3
UO	Uncombined oxides in clinker
<i>V</i>	Volume [cm^3]
V_m	Mass of water in first absorbed layer [g]
w_0/c_0	Water/cement ratio
<i>w</i>	Mass of reacted water [g]
w_0	Initial water mass
<i>x</i>	Mass fraction
<i>y</i>	Volume fraction

Greek

<i>v</i>	Specific volume [cm^3/g]
ρ	Density [g/cm^3]
φ	Volume fraction in (hydrated) paste
Φ	Volume fraction in hydration product
ω	Specific molar volume [cm^3/mol]

Subscript

<i>c</i>	Cement
cb	Chemically bound
cp	Capillary porosity
<i>d</i>	Compressed water (gel water + nonevaporable water)
<i>e</i>	Evaporable water (gel water + capillary water)
<i>g</i>	Gel
hc	Hydrated cement
hp	Hydration product (“gel”)
<i>n</i>	Nonevaporable
<i>p</i>	Porosity (capillary)
<i>s</i>	Shrinkage
<i>t</i>	Total
tp	Total porosity (capillary + gel porosity)
<i>w</i>	Capillary water
<i>x, y</i>	Molar ratios in chemical formulas

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Appendix A

Powers and Brownyard [1] observed that specific volume of the total water, v_t , decreases with increased hydration, implying shrinkage of the system. From section 2, it follows that

$$w_t v_t = w_t v_w + (v_d - v_w) w_d. \quad (\text{A.1})$$

Dividing by w_t and using Eq. (38):

$$v_t = v_w - B(v_w - v_d) \frac{w_n}{w_t}. \quad (\text{A.2})$$

Note that Powers and Brownyard [1] employed Eq. (A.2) with v_w set equal to $1 \text{ cm}^3/\text{g}$, a value which was assumed a priori (see discussion in section 2). The unit cm^3/g was omitted; in fact the computed values for $B(v_w - v_d)$ were not assigned with the dimension cm^3/g either. This omission finds its origin in Eq. (2) (Ref. [1], p. 671), where Eq. (A.2) is given, whereby 1 is used instead of v_w . $B(v_w - v_d)$ was computed by dividing $(1 - v_t)$ by w_n/w_t^3 . It appeared that for all examined cements, $B(v_w - v_d)$ takes averaged values between 0.245 and $0.290 \text{ cm}^3/\text{g}$ (Tables 5-1, 5-2, 5-3, 5-4, 5-5 and 5-6, pp. 673–681, Ref. [1]). An average value $0.279 \text{ cm}^3/\text{g}$ seemed most appropriate, yielding

$$\frac{v_t}{[\text{cm}^3/\text{g}]} = 1 - 0.279 \frac{w_n}{w_t}. \quad (\text{A.3})$$

Finally, Powers and Brownyard [1] assessed the magnitude of v_n and v_g by following an approximate approach. First, they reasoned that there is an upper limit to w_n/w_t . In case of no capillary water (i.e., $w_c = 0$), w_t only comprises nonevaporable (w_n) and gel water (w_g), i.e., $w_t = w_d$ and $v_t = v_d$, which is the minimum v_t (p. 688). As $w_n \approx w_g$ (Table 1) and, hence, $w_n/w_t = 0.5$, Eq. (A.3) yields $v_d = 0.861 \text{ cm}^3/\text{g}$.

Thus, this derivation is correct only in the special case that $B' = 1$ ($= w_n/w_g$, see Eq. (36)).

Subsequently, they determined the specific volume of the nonevaporable water by using a pycnometer and helium displacement measurements, carried out on P-dried samples. For all examined cements pastes, v_n did not vary that much: values of 0.81 to $0.83 \text{ cm}^3/\text{g}$ are measured, $0.82 \text{ cm}^3/\text{g}$ taken as representative value for all cements. Indirectly, the specific volume of the gel water could be determined by combining Eqs. (4) and (38):

$$v_g = \frac{(1 + B')v_d - v_n}{B'}. \quad (\text{A.4})$$

Assuming, again that w_n/w_g ($B' = 1$) and inserting $v_n = 0.82 \text{ cm}^3/\text{g}$ and $v_d = 0.86 \text{ cm}^3/\text{g}$, yields $v_g = 0.90 \text{ cm}^3/\text{g}$. Consequently, Powers and Brownyard [1] proposed

$$w_d v_d = w_n v_n + w_g v_g = 0.82 \text{ cm}^3/\text{g} w_n + 0.90 \text{ cm}^3/\text{g} w_g. \quad (\text{A.5})$$

The magnitude of v_n and v_g can also be obtained in a more rigorous way, as will be demonstrated here. The first step is to derive an expression for the specific volume of the “compressed water” (nonevaporable and gel water), v_d . This property can be obtained straightforward by combining Eqs. (A.2) and (A.3) and invoking $v_w = 1 \text{ cm}^3/\text{g}$:

$$v_d = 1 \text{ cm}^3/\text{g} - \frac{0.279 \text{ cm}^3/\text{g}}{B} = 1 \text{ cm}^3/\text{g} - \frac{0.279 \text{ cm}^3/\text{g}}{B' + 1}. \quad (\text{A.6})$$

Combining Eq. (A.6) with Eqs. (3), (4) and (38) now yields

$$w_d v_d = w_n v_n + w_g v_g = 0.721 \text{ cm}^3/\text{g} w_n + 1 \text{ cm}^3/\text{g} w_g. \quad (\text{A.7})$$

This relation is different from Eq. (A.5), the latter being valid only as long as w_n is close w_g . Moreover, in later work, the validity on the helium measurement and the consequential values of v_n ($0.82 \text{ cm}^3/\text{g}$) and v_g ($0.90 \text{ cm}^3/\text{g}$) have been doubted and $v_g = 0.9 - 1 \text{ cm}^3/\text{g}$ accepted [9,10].

In later publications, Copeland and Hayes [24] and Copeland [25] found experimentally that the best straight line for all examined cements could be fitted:

$$\frac{v_t}{[\text{cm}^3/\text{g}]} = 0.988 - 0.251 \frac{w_n}{w_t}. \quad (\text{A.8})$$

Thus, now, $v_w = 0.988 \text{ cm}^3/\text{g}$ and $B(v_w - v_d) = 0.251 \text{ cm}^3/\text{g}$. The lower value of v_w is owing to soluble constituents from the cement (alkalis and calcium hydroxide). It will be demonstrated that the fitted line and pertaining values for $B(v_w - v_d)$ are not conflicting with those from Powers and Brownyard [1].

In their work, the value of w_n/w_t was ranging from 0.550 to 0.242, whereby v_t was ranging from 0.850 to $0.942 \text{ cm}^3/\text{g}$, $v_t = 0.90 \text{ cm}^3/\text{g}$ being a representative value (Tables 5-1,

³ In fact: $(1 \text{ cm}^3/\text{g} - v_t)$ is divided by w_n/w_t .

5-2, 5-3, 5-4, 5-5 and 5-6, p. 673–681). Hence, if $(0.99 \text{ cm}^3/\text{g} - v_t)$, instead of $(1 \text{ cm}^3/\text{g} - v_t)$, would have been divided by w_n/w_t , values of $B(v_w - v_d)$ that are about 10% smaller would have been obtained. In other words, an average value of $0.251 \text{ cm}^3/\text{g}$, which is 90% of $0.279 \text{ cm}^3/\text{g}$, would have been found. This figure is identical to the value found by Copeland [25] (see Eq. (A.8)). Although this identical value is fortuitous, it confirms that, in essence, Powers and Brownyard [1] and Copeland [25] have measured the same shrinkage.

Using Eq. (A.2) and $v_w = 0.988 \text{ cm}^3/\text{g}$, the result of Copeland [25] yields

$$\begin{aligned} v_d &= 0.988 \text{ cm}^3/\text{g} - \frac{0.251 \text{ cm}^3/\text{g}}{B} \\ &= 0.988 \text{ cm}^3/\text{g} - \frac{0.251 \text{ cm}^3/\text{g}}{B' + 1}. \end{aligned} \quad (\text{A.9})$$

For $B' = 1$, $v_d = 0.863 \text{ cm}^3/\text{g}$. This implies that the specific volume of all compressed water is practically the same according to that of both Powers and Brownyard [1] and Copeland [25]. Subsequently, combining Eq. (A.9) with Eqs. (3), (4) and (38) now yields

$$\begin{aligned} w_d v_d &= w_n v_n + w_g v_g = 0.737 \text{ cm}^3/\text{g} w_n \\ &\quad + 0.988 \text{ cm}^3/\text{g} w_g. \end{aligned} \quad (\text{A.10})$$

Thus, these authors find that gel and capillary water are practically not compressed and having the same specific volume ($0.988 \text{ cm}^3/\text{g}$). This equation and the values of v_n and v_g are nearly equal to those involved with Eq. (A.7). All findings are in line with the foregoing discussion of dividing $(0.99 \text{ cm}^3/\text{g} - v_t)$ or $(1 \text{ cm}^3/\text{g} - v_t)$ by w_n/w_t , and the conclusion that the experiments of Powers and Brownyard [1] and Copeland [25] are in agreement.

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