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The work of Powers and Brownyard revisited: Part 2

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Abstract

Powers and Brownyard [Powers, T.C. and Brownyard, T.L., Studies of the physical properties of hardened Portland cement paste, Bull. 22, Res. Lab. of Portland Cement Association, Skokie, IL, U.S., 1948 reprinted from J. Am. Concrete Inst. (Proc.), Vol. 43 (1947), p. 101–132, p. 249–336, p. 469–505, p. 549–602, p. 669–712, p. 845–880, p. 933–992. [1]] were the first to systematically investigate the reaction of cement and water and the composition of cement paste. In Part I to this paper, their work was recapitulated (Brouwers [Brouwers, H.J.H., The work of Powers and Brownyard revisited: Part 1, accepted for publication in Cem. Concr. Res. 34 (2004) 1697–1716 [2]]). Here, it will be demonstrated that their water retention data also enables the study of the molar reactions of the aluminate (C_3A and C_4AF) and sulphate phases. It follows that the C_4AF most likely reacts with the C_3S and/or C_2S to form a Si containing hydrogarnet and portlandite. The remaining calcium silicates react to C–S–H ($C_{1.7}SH_{3.2}$ when saturated) and CH, as proposed in Part I [Brouwers, H.J.H., The work of Powers and Brownyard revisited: Part 1, accepted for publication in Cem. Concr. Res. 34 (2004) 1697–1716 [2]].

The $C\bar{S}$ seems to react exclusively with the C_3A. In case of carbonation, both phases react to hemi-carbonate, mono-sulphate, ettringite and tetra calcium aluminate hydrate. The concept “degree of carbonation” is introduced to quantify the fraction of mono-sulphate that is carbonated. This enables the quantification of all four hydration products, which represents a principal innovation. Subsequently, using the molar reactions and known specific volumes of the crystalline hydration products, the specific volumes of non-evaporable water (v_n) and gel water (v_g) are determined. These values are in line with the values suggested by Powers and Brownyard [Powers, T.C. and Brownyard, T.L., Studies of the physical properties of hardened Portland cement paste, Bull. 22, Res. Lab. of Portland Cement Association, Skokie, IL, U.S, reprinted from J. Am. Concrete Inst. (Proc.), Vol. 43 (1947), p. 101–132, p. 249–336, p. 469–505, p. 549–602, p. 669–712, p. 845–880, p. 933–992. [1]], which were based on their shrinkage data, implying a successful coupling of the molar reactions and their original paste model.

Keywords: Portland cement; Aluminate; Ferrite; Sulphate; Hydration

1. Introduction

In a pioneering work, Powers and Brownyard [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 (Fig. 1). 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.

In Refs. [2–4], Brouwers presented a rigorous review of their theoretical model and experimental results. Furthermore, it was 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. Using their model and data yields some major advantages. Firstly, in contrast to plain clinker hydration experiments, their experiments and model are based on a real cement–water system. In contrast to hydrating pure

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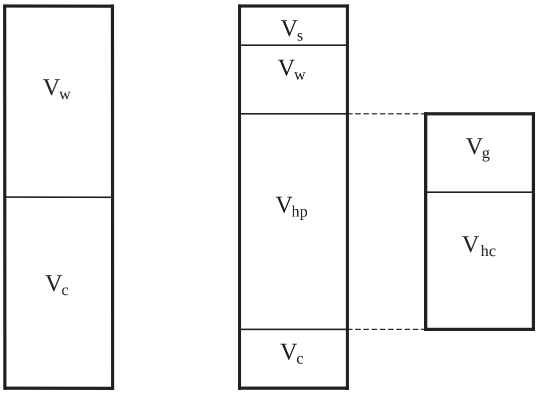

a) Initial situation b) Upon hydration

Fig. 1. Breakdown of cement paste and hydration product.

clinker minerals, a mix of clinker minerals that contain impurities, and that hydrate simultaneously, is more compatible with practice. Furthermore, their experiments concerned paste hydration, which is also closer to reality than bottle hydration experiments that are frequently reported. In Ref. [2], their results were applied to the hydration of the calcium silicate clinker phases. This application yielded the reaction stoichiometry, as well as the amount, density, porosity, water content, etc of the most abundant reaction product, C–S–H.

Likewise the approach of Le Chatelier, a picture that is generally accepted nowadays, the calcium silicate phases can be seen to react independently from the aluminate phase (Steinour [5]). Accordingly, in this paper the work of Powers and Brownyard [1] will be applied to the reactions of the aluminate, ferrite and sulphate phases. The type of products formed and their quantities can be derived from their water retention data. It will be seen that their classical work contains much more information and will have a wider application than is generally appreciated.

2. Water retention and shrinkage

As presented in Ref. [2], the model of Powers an Brownyard [1] specifies the amount of non-evaporable 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.

2.1. Non-evaporable water

For determining the non-evaporable water (w_n) P-drying was used, and the remaining non-evaporable 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" (p. 257–263).

It was noticed that w_n mainly depends on the clinker composition of the cements and the amount of reacted cement. Powers and Brownyard [1] fitted the following relation between w_n/c and the clinker composition:

$$w_n/c = 0.187\ x_{C_3S} + 0.158\ x_{C_2S} + 0.665\ x_{C_3A} + 0.213\ x_{C_4AF}. \tag{1}$$

Eq. (1) 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

$$m_{C_3S} = x_{C_3S}c;\ m_{C_2S} = x_{C_2S}c;\ \text{etc.}\ , \tag{2}$$

$$w = M_H\ n_H;\ m_{C_3S} = M_{C_3S}\ n_{C_3S};\ m_{C_2S} = M_{C_2S}\ n_{C_2S};\ \text{etc.}\ , \tag{3}$$

yielding

$$n_{H,n} = 2.37\ n_{C_3S} + 1.51\ n_{C_2S} + 9.97\ n_{C_3A} + 5.74\ n_{C_4AF}\ , \tag{4}$$

whereby the molecular masses of the clinker phases are taken from Table 1.

The non-evaporable water has also been determined by Copeland et al. [6], using both P-and D-drying for pastes matured for 1, 6.5 and 13 years. In Table 2 the coefficients of Copeland et al. [6] (by P-drying) are summarised. A glance at this Table 2 and Eq. (1) reveals that the non-evaporable water for the C_3S and C_2S are quite similar, but for the C_3A and C_4AF reactions deviating values are reported.

2.2. 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 RH, the water also condenses in the larger capillary pores. 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, that corresponds to 4 V_m per mass of reacted cement. This

Table 1
Properties of compounds

Substance	M (g/mol)	ρ (g/cm^3)	ω (cm^3/mol)
C_3S	228.33	3.120	73.18
C_2S	172.25	3.326	51.79
C_3A	270.20	3.060	88.30
C_4AF	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_3AH_6	378.32	2.527	149.71
C_6AFH_{12}	814.37	2.672	304.77
$C_6AFS_2H_8$	862.47	3.026	284.98
$C_6AFS_2H_{18}$	1042.67	2.241	465.18
$C_6AFS_4H_4$	910.57	3.431	265.40
C_2ASH_8	418.37	1.936	216.10
$C_4AFS_2H_{16}$	894.47	2.044	437.55
C_4AH_7	452.42	2.527	198.43
C_4AH_{13}	560.54	2.046	273.97
C_4AH_{19}	668.66	1.803	370.86
C_4AH_{22}	722.72	1.723	419.51
$C_4A\bar{S}H_{12}$	622.58	2.014	309.13
$C_4A\bar{S}H_{14}$	658.62	2.003	328.86
$C_4A\bar{C}_{0.5}H_{12}$	564.53	1.984	284.54
$C_4A\bar{C}H_{11}$	568.51	2.170	261.99
$C_6A\bar{S}_3H_{32}$	1255.26	1.775	707.04
$C_6A\bar{S}_3H_{36}$	1327.34	1.720	771.92

Densities are based on XRD data from Taylor [11,31], with the exception of the density of C_4AH_7, which is taken from Schwiete and Ludwig [14]. The properties of $C_6AFS_2H_{18}$, $C_4AFS_2H_{16}$, C_4AH_{22} and $C_6A\bar{S}_3H_{36}$ are based on the present work.

water quantity is retained at saturation, and water surplus to 4 V_m is capillary water [2]. 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 4 layers, the hydration product (gel space) is saturated. Based on a large number of carefully sorption experiments, Hagymassy et al. [7] measured that the amount absorbed at saturation is 4–5 times the amount adsorbed at a relative pressure of 20%, and that at saturation 5–6 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 non-evaporable water. This was explained by the fact that the internal surface of the hydration product is proportional to the amount of cement reacted. In view of this direct relation, Powers and Brownyard [1] introduced and measured the property V_m/w_n that was referred to as "k", accordingly:

$$w_g/w_n = B' = 4k = 4V_m/w_n \ . \tag{5}$$

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:

$$V_m/w_n = 0.230\ x_{C_3S} + 0.320\ x_{C_2S} + 0.317\ x_{C_3A} + 0.368\ x_{C_4AF}. \tag{6}$$

The constancy of w_g/w_n for a given cement is not a trivial result, and supports the viewpoint 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.

The total retained water, w_d/c, follows from Eq. (5) as

$$w_d/c = (1 + B')\ w_n/c = B\ w_n/c \ . \tag{7}$$

hereby B' and B were introduced, B' being the ratio w_g/w_n. From Refs. [1,2] it followed that the amount of gel water is almost equal to the amount of non-evaporable 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. (1) and (5)-(7), yielding:

$$w_d = 0.359\ m_{C_3S},\ w_d = 0.360\ m_{C_2S},\ w_d = 1.508\ m_{C_3A},\ w_d = 1.016\ m_{C_4AF}, \tag{8}$$

respectively. This result can be written in moles of water per mole of clinker phase using Eq. (3)

$$n_{H,d} = 4.55\ n_{C_3S},\ n_{H,d} = 3.44\ n_{C_2S},\ n_{H,d} = 22.6\ n_{C_3A},\ n_{H,d} = 14.2\ n_{C_4AF} \ . \tag{9}$$

As said, Powers and Brownyard [1] have expressed the gel water in the non-evaporable water. It enables the coupling of gel water (and hence, total retained water) to non-evaporable 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. (1)). 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. (1) and (6)). 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. (1)), which is a disadvantage of the chosen approach. Furthermore, the total retained water could also depend on the $C\bar{S}H_2$ content, so it is desirable to include this

Table 2
Coefficients to be used in Eq. (1) to determine chemically bound water following Copeland et al. [6]

Age	C_3S	C_2S	C_3A	C_4AF
1 year	0.228	0.168	0.429	0.132
6.5 years	0.234	0.178	0.504	0.158
13 years	0.230	0.196	0.522	0.109

mass fraction in a fit as well. Accordingly, a least squares method was employed [2,3] to the experimental data of Powers and Brownyard [1] to obtain

$$w_d/c = 0.334\ x_{C_3S} + 0.374\ x_{C_2S} + 1.410\ x_{C_3A} + 0.471\ x_{C_4AF} + 0.261\ x_{C\bar{S}}. \quad (10)$$

Likewise (as for the non-evaporable water), for the saturated state, the retained moles of water can now be expressed in moles of the clinker phases as well using Eqs. (2) and (3)

$$n_{H,d} = 4.23\ n_{C_3S} + 3.58\ n_{C_2S} + 21.1\ n_{C_3A} + 12.7\ n_{C_4AF} + 1.97\ n_{C\bar{S}}. \quad (11)$$

In Eq. (11) 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. (11) 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).

For each individual clinker phase, one can see that Eqs. (10) and (11) yield very similar values as provided by Eqs. (8) and (9), respectively. Eqs. (10) and (11) 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. (1) from Eq. (10) and Eq. (4) from Eq. (11), respectively:

$$w_g/c = 0.147\ x_{C_3S} + 0.216\ x_{C_2S} + 0.745\ x_{C_3A} + 0.258\ x_{C_4AF} + 0.261\ x_{C\bar{S}}, \quad (12)$$

$$n_{H,g} = 1.86\ n_{C_3S} + 2.07\ n_{C_2S} + 11.1\ n_{C_3A} + 6.96\ n_{C_4AF} + 1.97\ n_{C\bar{S}}. \quad (13)$$

For the saturated system, Eqs. (10)–(13) will be used henceforth.

2.3. Chemical shrinkage

In order 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 of Refs. [2,3] this work is summarized and it is shown that the results are in agreement with later work on this topic by Copeland and Hayes [8] and Copeland [9].

The specific volume of non-evaporable water, v_n, was found to be 0.72 cm^3/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 those formed by the aluminate bearing clinker phases. In Refs. [2,3] it was demonstrated that this value of v_n was also applicable to the hydration products formed by silicate bearing clinker phases.

The specific volume of the gel water and its possible compression (to 0.90 cm^3/g) has been subject of discussion (Powers and Brownyard [1], Copeland and Hayes [8], Copeland [9], Powers [10]), and up to now, the appropriate value of the effective specific volume is not decisively determined. But as we will see in the next two sections, for the crystalline reaction products the specific volumes are known, and v_g can be determined, yielding 0.90 cm^3/g. Also for the C–S–H there was enough supporting indications that the adsorbed ("gel") water is compressed to 0.90 cm^3/g [2,3].

3. Reactions of aluminate and sulphate phases

In contrast to the calcium silicate phases, which basically form CH and C–S–H, the aluminate phase can react in several ways with formation of several hydration products. In some reactions, calcium sulphate and carbon dioxide may also be involved. In contrast to the C–S–H gel, which is poorly crystalline to amorphous, the water content of most hydration products, which are (quasi-)crystalline, are known at a specified RH, as well as their specific volumes and other data. The structural water of these crystalline phases differs from the gel water of C–S–H. Like CH, these crystalline hydration products are impermeable and in the paste, their "gel" water (the water lost upon P-drying) cannot, like the C–S–H, be considered as gel space. In this section the reaction of aluminate and sulphate phases is discussed. It will be assumed a priori that the ferrite phase does not react with the sulphate phase; in the following Section the justification of this major assumption is presented.

Taylor [11] comprehensively reviews the hydration of C_3A. In water, C_3A will hydrate mainly to hydrogarnet (C_3AH_6). In a real water–cement system at room temperature, in the presence of calcium sulphate and calcium hydroxide, the aluminate hydrate C_4AH_{13-22} is formed from C_3A, CH and H; aluminate sulphate phases are also formed, such as $C_4A\bar{S}H_{12-14}$ (mono-sulphate) and $C_6A\bar{S}_3H_{32-36}$ (ettringite). Firstly, ettringite is formed, which then partly converts to mono-sulphate. This mono-sulphate is very susceptible to carbonation, resulting in the formation of ettringite and $C_4A\bar{C}_{0.5}H_{12}$ (hemi-carbonate). Only a few tenths of mass percent CO_2 in the cement mass is sufficient to prevent the presence of mono-sulphate. When sufficient CO_2 is present, hemi-carbonate can be replaced by the CO_2 richer mono-carbonate ($C_4A\bar{C}H_{11}$). For the present analysis, it is not important whether hemi-carbonate or mono-carbonate are formed, as the water retention by both substances is almost identical, so that here, attention is restricted to $C_4A\bar{C}_{0.5}H_{12}$.

Powers and Brownyard ([1], p. 261–263) were aware of these "microcrystalline" reaction products; $C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$ were designated low-sulphate and high-sulphate phases, respectively, of calcium sulfoaluminate. Furthermore, C_3AH_6 ("hexahydrate") was mentioned, but they also considered its existence in cement paste to be doubtful; the formation of hydrogarnet is therefore not considered here.

3.1. P-dried state

Powers and Brownyard ([1], p. 263) measured the formulae $C_4A\bar{S}H_{10}$ and $C_6A\bar{S}_3H_9$ for mono-sulphate and ettringite following P-drying, respectively. At 50 °C to 100 °C, which is roughly equivalent to P-drying in regard to hydration state, the aluminate hydrate and the hemi-carbonate take the mole ratios form C_4AH_{11} and $C_4A\bar{C}_{0.5}H_{10.5}$, respectively (Fischer and Kuzel [12]).

Hence, the (overall) reactions can be written as follows:

$$C_3A + CH + 10H \rightarrow C_4AH_{11}, \tag{14}$$

$$C_3A + 1/2CH + 1/2C\bar{C} + 10H \rightarrow C_4A\bar{C}_{0.5}H_{10.5}, \tag{15}$$

$$C_3A + C\bar{S}H_x + (10 - x)H \rightarrow C_4A\bar{S}H_{10}, \tag{16}$$

$$C_3A + 3C\bar{S}H_x + (9 - 3x)H \rightarrow C_6A\bar{S}_3H_9. \tag{17}$$

From Eqs. (14)–(17), it follows that, in P-dried state, each mole of hydrated C_3A retains about 10 mol of water, regardless of the product formed. Calcite, $C\bar{C}$, is taken as the CO_2 source for the formation of hemi-carbonate. It is formed by the weathering of cement and also appeared to be present in cements used by Powers and Brownyard [1]. This calcite is a major source of CO_2 for carbonation (Kuzel [13]). For the formation of aluminate hydrate/hemi-carbonate, 1/0.5 mole of CH is required, which is formed by the C_2S and C_3S reactions. So, for the formation of these reaction products, sufficient moles of C_2S and C_3S need to be present and react, which will be quantified later. Furthermore, the calcium sulphate phase may contain water and this water is available for subsequent reaction. If the value of x, the $H/\bar{S}$ ratio in the calcium sulphate, is zero, all four reactions (14)–(17) require about 10 mol of H per mole of C_3A reacted, being compatible with the value of 9.97 that follows from Eq. (4). Sulphate is already present in the cement clinker ($x=0$), and the former result would imply that the added sulphate (if any) was in the form of anhydrite ($C\bar{S}$) and/or as hemi-hydrate ($C\bar{S}H_{0.5}$, "plaster of Paris"), but none was added as gypsum ($C\bar{S}H_2$). It is possible that if gypsum was added, this gypsum was dehydrated to hemi-hydrate upon milling.

Copeland et al. [6] fitted a linear function relating the phase composition to retained water by D-and P-dried paste (the coefficients of the 4-parameter system are included in Table 2). They also determined the fit including the $C\bar{S}$ phase (a 5-parameter fit). Some fits indicate increased water retention with increasing $C\bar{S}$, but another fit, a decrease in water retention with increasing $C\bar{S}$. The trend was however weak, supporting the idea that for dried pastes the amount of $C\bar{S}$ has no major influence on retained water.

3.2. Saturated state

In the saturated state, the amount of retained water in relation to the moles of C_3A and $C\bar{S}$ is defined by Eq. (11), and is approximately:

$$n_{H,d} = 21n_{C_3A} + 2n_{C\bar{S}}\,. \tag{18}$$

In the absence of $C\bar{S}$ ($n_{C\bar{S}} = 0$) and in the presence of CH, only the aluminate hydrate and hemi-carbonate can be formed. The high water consumption renders the formation of hemi-carbonate unlikely, so from Eq. (18) it readily follows that in such case

$$C_3A + CH + 21H \rightarrow C_4AH_{22}. \tag{19}$$

This state of hydration is higher than given by Taylor [11], but in line with the C_4AH_{21} found by Le Chatelier in the 19th century (quoted by Schwiete and Ludwig [14]). Fischer and Kuzel [12] synthesised aluminate hydrates and with XRD, IR and DTA also measured the presence of C_4AH_{19} and found indications of hydrates with even more (inter-layer) water. At a RH lower than 80%, the hydrate is readily dehydrated to C_4AH_{13} (Schwiete and Ludwig [14]).

When sulphate is present, ettringite and mono-sulphate will be formed as well (Taylor [11]). In the presence of carbon dioxide, carbonation will occur, whereby mono-sulphate is unstable and reacts to form hemi-carbonate ($C_4A\bar{C}_{0.5}H_{12}$), and possibly also mono-carbonate ($C_4A\bar{C}H_{11}$). Sources of $\bar{C}$ are mixing water, ambient air and $C\bar{C}$ in the cement (Taylor [11], Kuzel [13]). Furthermore, in water saturated conditions, most likely $C_4A\bar{C}H_{11}$, $C_4A\bar{S}H_{14}$ and $C_6A\bar{S}_3H_{36}$ are formed (Kuzel [13], Dosch et al. [15], Pöllmann et al. [16], Pöllmann [17][1]. Using $x=0$ (i.e., an anhydrous sulphate phase), the following additional reactions are formulated:

$$C_3A + 1/2CH + 1/2C\bar{C} + 11.5H \rightarrow C_4A\bar{C}_{0.5}H_{12}, \tag{20}$$

$$C_3A + C\bar{S} + 14H \rightarrow C_4A\bar{S}H_{14}, \tag{21}$$

$$C_3A + 3C\bar{S} + 36H \rightarrow C_6A\bar{S}_3H_{36}. \tag{22}$$

The formation of hemi-carbonate has been assumed, but with the formation of mono-carbonate almost the same

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[1] At present, experiments take place to characterize the water stages of ettringite exceeding 32 molecules of water by using EXRD, thermal analysis, and KF titration [17].

amount of water is involved (11 moles of H instead of 11.5). Implicitly we assume that the initial mono-sulphate is able to consume all CO_2 and hence that mono-carbonate is not formed and that ettringite, the aluminate hydrate and the portlandite do not carbonate.

Computing which part of the C_3A is converted into C_4AH_{22}, $C_4A\bar{C}_{0.5}H_{12}$, $C_4A\bar{S}H_{14}$ and $C_6A\bar{S}_3H_{36}$, the mole balances of C_3A, $\bar{S}$ and H yield

$$n_{C_4AH_{22}} + n_{C_4A\bar{C}_{0.5}H_{12}} + n_{C_4A\bar{S}H_{14}} + n_{C_6A\bar{S}_3H_{36}} = n_{C_3A} \ , \tag{23}$$

$$n_{C_4A\bar{S}H_{14}} + 3n_{C_6A\bar{S}_3H_{36}} = n_{C\bar{S}} \, , \tag{24}$$

$$\begin{aligned}21n_{C_4AH_{22}} + 11.5n_{C_4A\bar{C}_{0.5}H_{12}} + 14n_{C_4A\bar{S}H_{14}} + 36n_{C_6A\bar{S}_3H_{36}} \\ = n_{H,d} = 21n_{C_3A} + 2n_{C\bar{S}} \, ,\end{aligned} \tag{25}$$

respectively, whereby Eq. (18) has been inserted. This set of three equations contains four unknowns. Decomposition of mono-sulphate also follows the equation:

$$\begin{aligned}3C_4A\bar{S}H_{14} + CH + C\bar{C} + 17H \rightarrow 2C_4A\bar{C}_{0.5}H_{12} \\ + C_6A\bar{S}_3H_{36} \, ,\end{aligned} \tag{26}$$

producing hemi-carbonate and ettringite (Taylor [11], Kuzel [13]). Note that Eq. (20) is the net result of Eqs. (21) and (26). So, the moles of ettringite produced and of mono-sulphate consumed are both related to the moles of hemi-carbonate formed. Accordingly, a degree of carbonisation, which is defined as the fraction of mono-sulphate that is converted in to hemi-carbonate is introduced:

$$n_{C_4A\bar{S}H_{14}} = (1-\alpha)n_{C_4A\bar{S}H^0_{14}} \ , \tag{27}$$

whereby the superscript "0" refers to the carbon dioxide-free condition. Considering Eq. (26), furthermore holds

$$n_{C_4A\bar{C}_{0.5}H_{12}} = \frac{2}{3}\alpha n_{C_4A\bar{S}H^0_{14}} \ , \tag{28}$$

$$n_{C_6A\bar{S}_3H_{36}} = n_{C_6A\bar{S}_3H^0_{36}} + \frac{1}{3}\alpha n_{C_4A\bar{S}H^0_{14}} \ . \tag{29}$$

Substituting Eqs. (27)–(29) into Eqs. (23)–(25) and solving the linear set of equations yields as an intermediate result

$$n_{C_4A\bar{S}H^0_{14}} = \left(\frac{9}{36-17\alpha}\right)n_{C\bar{S}} \ , \tag{30}$$

$$n_{C_6A\bar{S}_3H^0_{36}} = \frac{1}{3}\left(\frac{27-17\alpha}{36-17\alpha}\right)n_{C\bar{S}} \ , \tag{31}$$

and subsequently as the final result

$$n_{C_4AH_{22}} = n_{C_3A} - \frac{1}{3}\left(\frac{54-17\alpha}{36-17\alpha}\right)n_{C\bar{S}} \ , \tag{32}$$

$$n_{C_4A\bar{S}H_{14}} = \left(\frac{9(1-\alpha)}{36-17\alpha}\right)n_{C\bar{S}} \ , \tag{33}$$

$$n_{C_6A\bar{S}_3H_{36}} = \frac{1}{3}\left(\frac{27-8\alpha}{36-17\alpha}\right)n_{C\bar{S}} \ , \tag{34}$$

$$n_{C_4A\bar{C}_{0.5}H_{12}} = \frac{1}{3}\left(\frac{18\alpha}{36-17\alpha}\right)n_{C\bar{S}} \ . \tag{35}$$

In Eqs. (32)–(35), α is the degree of carbonation that prevailed during the experiments of Powers and Brownyard [1]. Most likely, as discussed in the foregoing, full carbonation of mono-sulphate occurred ($\alpha=1$), as is the case in most real pastes. If no carbonation had occurred $\alpha=0$ should be used in Eqs. (32)–(35), and another line of reasoning needs to be followed (Appendix B). So, it is assumed henceforth that the data of Powers and Brownyard [1] are based on carbonated pastes. According to Kuzel [13] this situation is most likely in practice as CO_2-free conditions are very difficult to achieve and only a little CO_2 is needed to prevent the formation of mono-sulphate. Under these conditions the amount of products formed follow from Eqs. (32)–(35) as

$$n_{C_4AH_{22}} = n_{C_3A} - \frac{37}{57}n_{C\bar{S}} \approx n_{C_3A} - \frac{2}{3}n_{C\bar{S}} \ , \tag{36}$$

$$n_{C_4A\bar{S}H^1_{14}} = 0 \ , \tag{37}$$

$$n_{C_6A\bar{S}_3H^1_{36}} = \frac{1}{3}n_{C\bar{S}} \ , \tag{38}$$

$$n_{C_4A\bar{C}_{0.5}H^1_{12}} = \frac{18}{57}n_{C\bar{S}} \approx \frac{1}{3}n_{C\bar{S}} \ , \tag{39}$$

respectively, whereby the superscript "1" refers to carbonation of all mono-sulphate.

For the full carbonation of mono-sulphate to hemi-carbonate, $n_{C\bar{C}}/n_{C\bar{S}}$ needs to be 1/6 (see Eq. (39)), or $m_{C\bar{C}}/m_{C\bar{S}}=12\%$ (molar masses taken from Table 1). So, related to the mass of calcium sulphate, only 12% of calcite is required for carbonation of all mono-sulphate. As the sulphate constitutes only a few percent of the cement mass, a few tenths of a percent of calcite in relation to cement mass is required, which is in line with findings in the literature (Taylor [11], Kuzel [13]). Ettringite and hemi-carbonate are stable (in contrast to mono-sulphate) and delayed ettringite formation is not likely when mono-sulphate is absent (Kuzel [13]).

Based on the previous analysis, it is also possible to assess the quantities of hydration products formed in cement pastes with any given degree of carbonation. To this end, Eqs. (28)–(39) yield

$$n_{C_4A\bar{S}H_{14}} = \frac{9}{19}(1-\alpha)n_{C\bar{S}} \approx \frac{1}{2}(1-\alpha)n_{C\bar{S}} \ , \tag{40}$$

$$n_{C_4A\bar{C}_{0.5}H_{12}} = \frac{6}{19}\alpha n_{C\bar{S}} \approx \frac{1}{3}\alpha n_{C\bar{S}} \ , \tag{41}$$

$$n_{C_6A\bar{S}_3H_{36}} = \frac{1}{57}(10+9\alpha)n_{C\bar{S}} \approx \frac{1}{6}(1+\alpha)n_{C\bar{S}} \ , \tag{42}$$

in which α is the degree of carbonation of the paste. For all α, the amount of C_4AH_{22} follows from Eq. (36) as carbonation only affects the three other hydration products. From Eq. (36) and Eqs. (40)–(42) one can compute the water retention at arbitrary carbonation. Considering the water retention of each substance and their quantity (expressed in n_{C_3A} and $n_{C\bar{S}}$) yields as water retention by all hydration products formed by aluminate and sulphate

$$n_{H,d} = 21\ n_{C_3A} + 2\left(\frac{51\alpha-13}{38}\right)n_{C\bar{S}} \approx 21\ n_{C_3A} + 2\left(\frac{4}{3}\alpha-\frac{1}{3}\right)n_{C\bar{S}} \ . \tag{43}$$

From this equation, it follows that the coefficient pertaining to $n_{C\bar{S}}$ is equal to 2 when $\alpha=1$, i.e., full carbonation, in accord with Eqs. (11) and (18). But, when partial carbonation occurs ($\alpha<1$), the water retention is decreased, because less conversion of mono-sulphate to hemi-carbonate and ettringite implies less water retention; see Eq. (26). For $\alpha\approx 1/4$, there is no dependence of water retention on sulphate content; likewise the water retention in P-dried state. For $\alpha<1/4$, the water retention correlates negatively with the sulphate contents.

From Eqs. (40)–(42) the following quantitative conclusions follow. The moles of mono-sulphate, hemi-carbonate (plus possibly mono-carbonate) and ettringite formed depend on $n_{C\bar{S}}$, but their ratio is constant and depends only on the degree of carbonation:

$$\frac{n_{C_4A\bar{C}_{0.5}H_{12}}}{n_{C_6A\bar{S}_3H_{36}}} = \frac{18\alpha}{10+9\alpha} \approx \frac{2\alpha}{1+\alpha} \ , \tag{44}$$

$$\frac{n_{C_4A\bar{S}H_{14}}}{n_{C_6A\bar{S}_3H_{36}}} = \frac{27(1-\alpha)}{(10+9\alpha)} \approx \frac{3(1-\alpha)}{(1+\alpha)} \ . \tag{45}$$

For full carbonation of the mono-sulphate ($\alpha=1$), as assumed to prevail during the experiments of Powers and Brownyard [1] and in most practical cases, the molar ratio of hemi-carbonate and ettringite is about unity. In a CO_2-free environment (laboratory conditions, $\alpha=0$), the moles of mono-sulphate and ettringite formed have a ratio of about three. This ratio changes dramatically even in case of slight carbonation: e.g., for $\alpha=1/2$ this ratio readily drops to unity. This is due on the one hand to the consumption of mono-sulphate and on the other, to the formation of ettringite.

The mass ratio can be computed by combining Eqs. (44) and (45) using the molar masses from Table 1:

$$\frac{m_{C_4A\bar{C}_{0.5}H_{12}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \frac{7\alpha}{10+9\alpha} \ , \tag{46}$$

$$\frac{m_{C_4A\bar{S}H_{14}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \frac{3(1-\alpha)}{2(1+\alpha)} \ , \tag{47}$$

respectively. In a fully carbonated the system, the mass ratio of ettringite to hemi-carbonate is about 2.7, and in a CO_2-free system, the mass ratio of ettringite to mono-sulphate is about 2/3.

The hemi-carbonate and mono-sulphate formed are expressed by the amount of ettringite formed, as this latter product is always present if sulphate is present. The ratios appear not to depend on either n_{C_3A} or $n_{C\bar{S}}$. It is interesting to determine the ratio of tetra calcium aluminate hydrate to ettringite: combining Eqs. (36) and (42) yields:

$$\frac{n_{C_4AH_{22}}}{n_{C_6A\bar{S}_3H_{36}}} = \left[\frac{57}{10+9\alpha}\right]\left[\frac{n_{C_3A}}{n_{C\bar{S}}}-\frac{37}{57}\right] \approx \left[\frac{6}{1+\alpha}\right]\left[\frac{n_{C_3A}}{n_{C\bar{S}}}-\frac{2}{3}\right] \ . \tag{48}$$

One can readily see that the first factor on the right-hand side is equal to three for the carbonated system and six for the CO_2-free system. Using the molar masses listed in Table 1, this equation can be expressed as

$$\frac{m_{C_4AH_{22}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \left[\frac{3}{2(1+\alpha)}\right]\left[\frac{x_{C_3A}}{x_{C\bar{S}}}-\frac{4}{3}\right] \tag{49}$$

Apparently, irrespective of the degree of carbonation, the number of moles C_3A (n_{C_3A}) necessary to bind all sulphate (i.e., so that no aluminate hydrate is formed) needs to be 2/3 the number of moles of $C\bar{S}$ ($n_{C\bar{S}}$). This corresponds to a mass ratio $m_{C\bar{S}}/m_{C_3A}$ (or $x_{C\bar{S}}/x_{C_3A}$) of about 3/4. If all sulphate were added as gypsum, $x_{C\bar{S}}$ in Eq. (49) needs to be replaced by $0.8x_{C\bar{S}H_2}$ to account for their molar masses (Table 1).

The computed minimum value for $n_{C_3A}/n_{C\bar{S}}$ (=2/3) is larger than the value expected if all C_3A were converted into ettringite, namely 1/3. This is due to the fact that mono-carbonate is formed simultaneously during carbonation, which is consuming aluminate. On the other hand, in a CO_2-free environment, the computed minimum value for $n_{C_3A}/n_{C\bar{S}}$ (=2/3) is smaller than the value that one would expect if all C_3A would be converted into mono-sulphate, namely unity. Now the difference is caused by the ettringite, which binds 3 moles of $C\bar{S}$ per mole of C_3A.

The water retention data of Powers and Brownyard [1], application to Eqs. (19)–(22) and the assumption that full carbonation occurred leads to quantitative predictions of the four reaction products in both a carbonating and a CO_2-free system. From the P-dried analysis, it is concluded here that during the experiments reported by Powers and Brownyard [1], the sulphate phase was present as $C\bar{S}$, i.e., $x=0$ and that full carbonation of mono-sulphate has occurred. It is believed that if (part of) the sulphate is added as hemi-hydrate ($x=1/2$) or gypsum ($x=2$) and/or carbonation is (partly) prevented, the quantities of products formed will not change significantly. In that case, the extra water introduced in the paste by these two water-bearing sulphate phases must be accounted for. In the case of 5% (mass) gypsum added (which consists of about 20% (mass) water, Table 1), the cement will bear 1% (mass) water. When the $w_0/c_0=0.40$, it is actually $0.41/0.99\approx 0.42$.

To form aluminate hydrate and hemi-carbonate, portlandite is required (Eqs. (19) and (20)); it results from the C_2S and/or C_3S reactions [2]. Each mole of C_2S and C_3S produce 0.3 and 1.3 moles of CH, respectively. As 1 mole of hydrate/hemi-carbonate requires 1/0.5 mole of CH, it follows that

$$0.3n_{C_2S}+1.3n_{C_3S}\geq n_{C_4AH_{22}}+0.5n_{C_4A\bar{C}_{0.5}H_{12}}\approx n_{C_3A}-n_{C\bar{S}}\left(\frac{2}{3}-\frac{1}{6}\alpha\right), \qquad (50)$$

which is applicable both in a carbonating and in a CO_2-free environment. If Eq. (50) is fulfilled, the aluminate hydrate and hemi-carbonate always can be formed. Note that the required amount of calcium silicates (and portlandite) is reduced when $C\bar{S}$ is present. In its presence, not all C_3A is converted into the hydrate, and obviously less CH is required, even when hemi-carbonate is formed. With Eqs. (2) and (3), and the molar masses in Table 1, Eq. (50) can also be written in cement mass fractions as:

$$0.47x_{C_2S}+1.54x_{C_3S}\geq x_{C_3A}-x_{C\bar{S}}\left(\frac{4}{3}-\frac{1}{3}\alpha\right). \qquad (51)$$

In case sulphate is added in the form of gypsum and the mass fraction of gypsum is specified, $x_{C\bar{S}}$ needs to be replaced by $0.8\,x_{C\bar{S}H_2}$ (Table 1). In Ref. [2] it was confirmed that for all investigated cements, condition (51) has been fulfilled, so that the reaction mechanism proposed here does not contradict the underlying experiments. Furthermore, as CEM I requires $x_{C_2S}+x_{C_3S}\geq 2/3$, the reaction mechanism is applicable to all CEM I.

3.3. Compressed water

The definitions by Powers and Brownyard [1] and the densities and molar mass of the reaction products in P-dried and saturated states enable the determination of specific volume of non-evaporable water (v_n) and gel water (v_g).

Subtracting the volume of 1 mole of C_3AH_6 and 1 mole of C_3A yields 61.41 cm^3 (Table 1), corresponds in the concept by Powers and Brownyard [1] to the volume of 6 moles of reacted water (non-evaporable water). This implies that this water has a specific molar volume $\omega_{H,n}=10.23$ cm^3/mole, corresponding to $v_n=0.57$ cm^3/g. This value is much lower than found by Powers and Brownyard [1] and Copeland [9], and is a consequence of the extreme shrinkage involved with the hydration reaction. The formation of 1 mole of hydrogarnet consumes 6 moles of water. This magnitude is not in line either with the water retention pertaining to C_3A, which indicate the retention of about 21 moles of water in saturated state, and the retention of 10 moles H per mole of C_3A in P-dried state. Even if one would assume that the C_3AH_6 is quasi-crystalline and would be able to bind another 6 moles of water per mole C_3AH_6 (being gel water and removable by P-drying), the disagreement with expected water retention is too large. The modest water retention and the substantial shrinkage render the formation of C_3A not very likely, confirming the finding of previous researchers that this product is not formed in cement paste (Powers and Brownyard [1], Taylor [11], Copeland et al. [18]), and discussed at the beginning of this Section.

Likewise for the tetra calcium aluminate hydrate, the densities of the retained water can be computed. To this end, in Table 1 also dehydrated forms of C_4AH_{22} are included (C_4AH_7, C_4AH_{13} and C_4AH_{19}), the density of C_4AH_{22} is not yet known. In line with the definitions by Powers and Brownyard [1], determination of the specific volume of the non-evaporable (v_n) and/or gel water (v_g) is possible. Subtracting the volume of 1 mole of C_4AH_{13} from the volume of 1 mole of C_4AH_{19} yields 96.89 cm^3 (Table 1), which comprises the volume of 6 moles of retained water. This water has a specific molar volume of 16.15 cm^3/mole, implying a specific density of 0.90 cm^3/g. This water will be lost during P-drying. Furthermore, subtracting the volume of 1 mole of C_4AH_7 from 1 mole of C_4AH_{13} yields 75.54 cm^3 (Table 1). This volume again comprises the volume of 6 moles of retained water. This implies that this water has a specific molar volume of 12.59 cm^3/mole, or a specific volume of 0.70 cm^3/g. A part of this water is removed by P-drying (from C_4AH_{13} to C_4AH_{11}), being gel water, the rest on ignition (from C_4AH_{11} to C_4AH_7), being non-evaporable water. The involved compression is thus better accounted for when the gel water is compressed as well. Considering all degrees of hydration, the gel water is compressed, so $v_n=0.72$ cm^3/g and $v_g=0.90$ cm^3/g are good values for water in the aluminate hydrate.

To determine the compression of the water involved in the formation of mono-sulphate, the molar volumes of the reactants are subtracted from the reaction products appearing in Eq. (21), and the molar volumes are taken from Table 1. This yields 187.34 cm^3, which corresponds to the volume of 14 moles of water involved in the reaction. Hence, the mean specific molar volume of the water reads 13.38 cm^3/mole, corresponding to a mean specific volume $v_d=0.74$ cm^3/g for all water involved in the reaction. This is the mean specific volume of non-evaporable (10/14) and gel water (4/14), see Eqs. (16) and (21). The term “gel water” is used, as it is water that will be lost upon P-drying, but actually it is structural interlayer water. Using $v_n=0.72$ cm^3/g and $v_g=1$ cm^3/g, as average $v_d=0.80$ cm^3/g is obtained, which does not match with $v_d=0.74$ cm^3/g (based on the reaction). On the other hand, using $v_n=0.72$ cm^3/g and $v_g=0.9$ cm^3/g, as average $v_d=0.77$ cm^3/g is obtained, being in better agreement with the previously determined value based on the reaction scheme.

The same procedure can be carried out for the ettringite reaction. As the density of $C_6A\bar{S}_3H_{36}$ is not known yet, the formation of $C_6A\bar{S}_3H_{32}$ is studied instead. In that case, the difference in volume of the solids appearing in Eq. (22) yields a volume of 477.62 cm^3, which corresponds to the volume of 32 moles of reacting water. Hence, the specific molar volume for the retained water becomes 14.93 cm^3/mole and its mean specific volume is 0.83 cm^3/g. In contrast to mono-sulphate, the largest part of the water will be lost upon P-drying, being "gel water" (23/32), and the minor part is non-evaporable water (9/32), see Eqs. (17) and (22). Using $v_n=0.72$ cm^3/g and $v_g=1$ cm^3/g, as average $v_d=0.92$ cm^3/g is obtained, which is not compatible with the previously determined value based on the reaction. On the other hand, when also the gel water is compressed (likewise the hydrate and mono-sulphate), so using $v_n=0.72$ cm^3/g and $v_g=0.90$ cm^3/g, now as average $v_d=0.85$ cm^3/g is obtained, which corresponds better to the compression involved with the reaction.

Finally, the water involved with the hemi-hydrate reaction is considered. The molar volumes of the reactants are subtracted from the reaction products appearing in Eq. (20). This computation yields 161.26 cm^3, corresponding to the volume of 11.5 moles of water involved in the reaction. Hence, the specific molar volume of the water is 14.02 cm^3/mol, corresponding to a mean specific volume $v_d=0.78$ cm^3/g. This is the mean specific volume of non-evaporable (10/11.5) and gel water (1.5/11.5), see Eqs. (15) and (20). Using $v_n=0.72$ cm^3/g and $v_g=1$ cm^3/g results in $v_d=$ 0.76 cm^3/g, which is in good agreement with the previously determined value based on reaction (20). Using $v_n=0.72$ cm^3/g and $v_g=0.9$ cm^3/g on the other hand, an average $v_d=0.74$ cm^3/g is obtained, which is in slightly worse agreement with the previously determined value based on reaction (20). So, uncompressed gel water gives better agreement only for the formation reaction of hemi-hydrate.

These analyses of the water retained by the four reaction products leads to the conclusion that v_n has a density of about 0.72 cm^3/g, which is in line with the density of the non-evaporable water of the other reaction products C–S–H and CH (Brouwers [2,3]). This is also in line with the finding of Powers and Brownyard [1], discussed by Brouwers [2,3]. The gel water retained by the hemi-hydrate, takes a value of 1 cm^3/mol. For the gel water of the aluminate hydrate, the mono-sulphate and the ettringite, on the other hand, $v_g=0.90$ cm^3/g seems more appropriate. The hemi-hydrate binds only a minor part of the total gel water in the hydration product, see Eqs. (36) and (40)-(42), even when $n_{C\bar{S}}/n_{C_3A}$ is large and $\alpha=1$ (the maximum). Accordingly, $v_n=0.72$ cm^3/g and $v_g=0.90$ cm^3/g is most appropriate for the reaction products formed by the reaction of C_3A with $C\bar{S}$, CH and water.

4. Reaction of ferrite phase

The clinker phases C_3S, C_2S and C_3A were already known to Le Chatelier in 1887. The ferrite phase, on the other hand, was discovered later, in 1928 according to Steinour [5]. The hydration of this phase, which is the most variable in composition, still raises questions. First of all, distinction needs to be made between the reaction of the pure synthetic phase at one hand, and the reaction of the impure phase as found in cement clinker, reacting in the presence of the other clinker phases (Taylor [11]). Collepardi et al. [19], Fukuhura et al. [20], Emanuelson and Hansen [21] describe the hydration of synthetic ferrite, but ferrite in clinker may be more complex.

It is reported that similar products can be formed from ferrite as from C_3A, such as mono-sulphate, hydrate and ettringite, in which Al is partly substituted by Fe (Taylor [11], Schwiete and Ludwig [14]). The partial replacement of Al by Fe in ettringite, yielding approximately $C_6A_{0.75}F_{0.25}\bar{S}_3H_{31}$, however, has only been found by hydration of synthetic ferrite and $C\bar{S}$ (Collepardi et al. [19], Fukuhara et al. [20]). The formation of FH_3 has not been detected either in real cement pastes, though it could be amorphous and therefore difficult to detect. These findings render the similarity between C_3A and C_4AF reactions distant (Taylor [11]). These reactions will be considered here, but it will be seen that the water retention results of Powers and Brownyard [1] will render their occurrence unlikely.

In real cement pastes, on the other hand, Fe has been found in hydrogarnets. Flint et al. [22] synthesized hydrogarnets of composition $C_6AFS_xH_{12-2x}$ ($0 \leq x \leq 6$), being solid solutions of $C_3AS_{x/2}H_{6-x}$–$C_3FS_{x/2}H_{6-x}$ and suggested that this product could be formed by the hydration of C_4AF and calcium silicates in cement. Using XRD, Copeland et al. [18] and Kantro et al. [23] indeed suspected a phase with an approximate composition $C_6AFS_2H_8$ in hydrated cement. In a pure system of C_3S and C_4AF, Schwiete and Iwai [24] found that with increasing C_3S/C_4AF, the S/F ratio (x) in the formed $C_6AFS_xH_{12-2x}$ also increased, but that the value of x did not exceed 2 (at room temperature). For $x>1.5$ the hydrogarnet was stable to sulphate attack with practically no transition to ettringite. Using XRD and EMPA, Taylor and Newbury [25] confirmed the presence of a hydrogarnet close to $C_6A_{1.2}F_{0.8}S_2H_{18}$ in hydrated Portland cement. Based on SEM and TEM, Rodger and Groves [26] suggested a composition of $C_6A_{0.6}F_{0.6}S_2H_x$ in Portland cement and cement–fly ash blends. Paul and Glasser [27] investigated Portland cement pastes that underwent prolong cure (8.4 years) at 85 °C, which has however limited predictability towards cement hydration at ambient temperature; using XRD and DTA/TGA, they estimated that the observed hydrogarnet in their paste had a composition close to $C_6A_{1.26}F_{0.51}M_{0.46}S_{2.8}\bar{S}_{0.58}H_{5.59}$. The possible formation of these Fe and Si containing hydrogarnets will also be investigated here.

4.1. P-dried state

Assuming that the water retention of the Fe substituted substances exhibit the same water retention as their Al counterparts (previous Section), the equivalent C_4AF hydration reactions can be written as follows:

$$C_4AF + 14H \rightarrow C_4(A_{1-x},F_x)H_{11} + (F_{1-x},A_x)H_3, \qquad (52)$$

$$C_4AF + C\bar{S}H_y + (14-y)H \rightarrow C_4(A_{1-x},F_x)\bar{S}H_{10} + CH + (F_{1-x},A_x)H_3, \qquad (53)$$

$$C_4AF + 3C\bar{S}H_y + (13-3y)H \rightarrow C_6(A_{1-x},F_x)\bar{S}_3H_9 + CH + (F_{1-x},A_x)H_3. \qquad (54)$$

For reactions (52)–(54), each mole of C_4AF requires 4 more moles of water than for the corresponding reaction of 1 mol of C_3A (compare with Eqs. (14), (16) and (17). This difference is due to the formation/consumption of 1 mole of CH, and the formation of 3 moles of $(F_{1-x},A_x)H_3$ per mole C_4AF. Eq. (4) reveals however, that 1 mole of C_4AF retains only 5.74 moles of water, which is less than the 9.97 moles of water retained by 1 mole of C_3A. This finding renders the occurrence of reactions (52)–(54) doubtful (to say the least).

The formation of hydrogarnet can be represented as follows

$$C_4AF + xC_2S + (2x+y-2)H \rightarrow C_6AFS_xH_y + (2x-2)CH, \qquad (55)$$

$$C_4AF + xC_3S + (3x+y-2)H \rightarrow C_6AFS_xH_y + (3x-2)CH. \qquad (56)$$

In P-dried state, for the hydrogarnet furthermore holds

$$2x + y = 12\ . \qquad (57)$$

And from Eq. (4) follows

$$n_{H,n} = 1.51 n_{C_2S} + 2.37 n_{C_3S} + 5.74 n_{C_4AF}\ . \qquad (58)$$

Applying Eq. (57) to Eq. (55) yields $n_{H,n}=10$. Furthermore, $n_{C_2S}=x$, $n_{C_3S}=0$ and $n_{C_4AF}=1$. Substitution of these values and $n_{H,n}=10$ into Eq. (58) yields $x=2.8$, and Eq. (57) then yields $y=6.4$. Applying (57) to Eq. (56) yields $n_{H,n}=10+x$; combining this with $n_{C_2S}=0$, $n_{C_3S}=x$ and $n_{C_4AF}=1$, and substituting into Eq. (58) yields $x=3.1$. With Eq. (57), $y=5.8$ is obtained.

The calculated compositions of the hydrogarnets are very close (an S/F ratio of about 3), irrespective if the silicon originates from C_2S or C_3S, and their composition comes close to composition that has been measured by the authors mentioned above. The analysis here supports the idea that in the pastes of Powers and Brownyard [1] C_4AF has reacted with C_2S and/or C_3S to form hydrogarnet, than that C_4AF has reacted with water and/or $C\bar{S}$ according to Eqs. (52)–(54). The absence of Fe and sulphur containing phases could be due to the fact that C_3A reacts more rapidly than C_4AF, and therefore C_3A might consume all sulphate in the cement system.

As previous authors found an S/F ratio of 2 at ambient temperatures, the C_4AF and calcium silicates most likely react to $C_6AFS_2H_8$. The physical properties of this form can be found in Table 1. Note that if the coefficient 5.74 appearing in Eq. (58) would only have been 25% larger (i.e., a water retention of about 7.14 moles of water per mole C_4AF instead of 5.74), $x \approx 2$ would have been obtained from the present analysis indeed.

4.2. Saturated state

From literature and the P-dried water retention results it followed that most likely a hydrogarnet of composition near $C_6AFS_2H_8$ is formed. Here, using the data on water retention of saturated paste, the hydration reaction of C_4AF is investigated.

Using the same water retention as the saturated Al containing products (Section 3), the following reactions occur:

$$C_4AF + 22-25H \rightarrow C_4(A_{1-x},F_x)H_{19-22} + (F_{1-x},A_x)H_3, \qquad (59)$$

$$C_4AF + C\bar{S}H_y + (18-y)H \rightarrow C_4(A_{1-x},F_x)\bar{S}H_{14} + CH + (F_{1-x},A_x)H_3, \qquad (60)$$

$$C_4AF + 3C\bar{S}H_y + (40-3y)H \rightarrow C_6(A_{1-x},F_x)\bar{S}_3H_{36} + CH + (F_{1-x},A_x)H_3. \qquad (61)$$

Eq. (59) is not very likely as this water retention is not compatible with Eq. (11). Even if the water contribution by the $C\bar{S}$ term is considered (Eq. (11)),

$$n_{H,d} = 12.7\, n_{C_4AF} + 1.97\, n_{C\bar{S}}\ , \qquad (62)$$

the retained water as predicted by Eq. (62) is far from sufficient to enable reaction (61). On the other hand, Eq. (62) prescribes a water retention of nearly 15 H for Eq. (60). If one would assume that all sulphate was present as gypsum (not very likely), the left-hand side of reaction (60) would contain 16 H as $y=2$, which is close to the water retention of 15 H that follows from Eq. (62). However, the P-dried analysis rendered Eqs. (59)–(61) unlikely. Furthermore, it has been observed that F substituted mono-sulphate (in contrast to ettringite) is not likely to be formed (Fukuhura et al. [20]). So, the water retention correlation for saturated paste yields the same conclusion as the water retention correlation in P-dried state: in cement paste C_4AF appears not to react according to Eqs. (59)–(61).

Using the values for x (2 or 3) as obtained from the analysis of the P-dried state, the hydrogarnet reactions in saturated state can be modelled by Eqs. (55) and (56)), whereby y is yet unknown. Similarly as for the aluminate hydrate in the previous Section, which appeared to retain extra interlayer water, the hydrogarnet will be allowed to retain more water than prescribed by Eq. (57).

From Eq. (11) follows the water retention in saturated state

$$n_{\mathrm{H,d}} = 3.58n_{\mathrm{C_2S}} + 4.23n_{\mathrm{C_3S}} + 12.74n_{\mathrm{C_4AF}} \;. \qquad (63)$$

Applying $x=2$ to Eq. (55) yields $n_{\mathrm{H,d}}=2+y$, $n_{\mathrm{C_2S}}=2$, $n_{\mathrm{C_3S}}=0$ and $n_{\mathrm{C_4AF}}=1$. Substitution of these values into Eq. (63) yields $2+y=19.92$ and hence, $y=17.92$ (i.e., $C_6AFS_2H_{17.92}$ is formed). Applying $x=2$ to Eq. (56) yields $n_{\mathrm{H,d}}=4+y$, $n_{\mathrm{C_2S}}=0$, $n_{\mathrm{C_3S}}=2$ and $n_{\mathrm{C_4AF}}=1$. Substitution of these values into Eq. (63) yields $4+y=21.2$ and hence, $y=17.2$ ($C_6AFS_2H_{17.2}$ is formed). In comparison to dried hydrogarnet ($C_6AFS_2H_8$), saturated hydrogarnet per mole apparently retains 9 to 10 moles of water more. When the same procedure is also carried out with $x=3$, then $C_6AFS_3H_{19.48}$ and $C_6AFS_3H_{18.43}$ follows from the reactions with C_2S or C_3S, respectively. Also in these cases the saturated hydrogarnet holds 12 to 13 more moles of water than in dried state ($C_6AFS_3H_6$).

This high water retention by the hydrogarnet could be caused by the formation of very small crystals and/or imperfectly ordered structures [31]. Another explanation is that actually a Fe-substituted gehlenite hydrate ($C_2A_{0.5}F_{0.5}SH_8$) is formed in a saturated paste, which together with CH, is transformed into a hydrogarnet upon (P-) drying. The analogue reaction of unstable C_2ASH_8 and CH to C_3ASH_4, is explained by Damidot and Glasser [28] using a phase diagram, a transition that was observed by Locher [29] as well. This transition upon drying would read

$$C_4AFS_2H_{16} + 2CH \rightarrow C_6AFS_2H_8 + 10H. \qquad (64)$$

If gehlenite hydrate is formed in saturated state, the reaction would read

$$C_4AF + 2C_2S + 20H \rightarrow C_4AFS_2H_{16} + 4CH, \qquad (65)$$

$$C_4AF + 2C_3S + 22H \rightarrow C_4AFS_2H_{16} + 6CH. \qquad (66)$$

However, it should be noted that this Fe-substituted gehlenite hydrate has, to the author's knowledge, never been observed in Portland cement paste. It has been observed only in the gehlenite hydrate produced by slag blended aluminate cements (Rayment and Majumbar [30]). In Portland cement only the Fe substituted hydrogarnet has been observed (see beginning of this Section), in pastes that are usually dried to some extent upon experimental analysis. For the same reason usually also C_4AH_{13}, $C_4A\bar{S}H_{12}$ and $C_6A\bar{S}_3H_{32}$ are detected, and not C_4AH_{19-22}, $C_4A\bar{S}H_{14}$ and $C_6A\bar{S}_3H_{36}$, which can persist only in saturated state (Fischer and Kuzel [12], Kuzel [13], Dosch et al. [15], Pöllmann et al. [16],). In this regard it is also interesting to note that Powers and Brownyard [1] mention the presence of the hydrogarnet C_3AH_6 with comparable higher water retention (C_3AH_{12} or $C_6A_2H_{24}$). In later work, however, this product appeared to be mono-carbonate ($C_4A\bar{C}H_{11}$) (Taylor [11], [31]). To conclude, the water retention experiments by Powers and Brownyard [1] on real cement pastes and the analysis there from here, confirm the formation of supersaturated hydrogarnet and/or gehlenite hydrate (in saturated state) and hydrogarnet (P-dried state).

To form the hydrogarnet/gehlenite hydrate, S is involved (Eqs. (55), (56), (65) and (66)), which is provided by C_2S and/or C_3S. As 1 mole of hydrogarnet/gehlenite hydrate requires 2 moles of S and 1 mole of C_4AF, it follows that if

$$n_{\mathrm{C_2S}} + n_{\mathrm{C_3S}} \geq 2n_{\mathrm{C_4AF}} \;, \qquad (67)$$

the hydrogarnet/gehlenite hydrate can be formed. With the help of Eqs. (2) and (3), and the molar masses listed in Table 1, Eq. (67) can also be written in cement mass fractions

$$1.41x_{\mathrm{C_2S}} + 1.06x_{\mathrm{C_3S}} \geq x_{\mathrm{C_4AF}} \;. \qquad (68)$$

For most cements condition (68) will be fulfilled [2], so that the reaction mechanism proposed here is not in contradiction with the underlying experiments. Even when the formation of a hydrogarnet with $S/F=3$ is assumed (in that case the two coefficients on the left-hand sides of Eqs. (67) and (68) should both be multiplied by 2/3), the hydrogarnet reaction is possible.

C_4AF consumes C_2S and/or C_3S to form the crystalline hydrogarnet/gehlenite hydrate, and consequently, less C–S–H gel is formed. On the other hand, with the formation of hydrogarnet/gehlenite hydrate both C_2S and C_3S produce per mole more CH than with the formation of C–S–H (no C_4AF involved). This can easily be verified by considering Eqs. (55) and (56) (with $x=2$) and Eqs. (65) and (66) at one hand, and "Eqs. (45) and (46)" from [2] with $x<2$ (e.g., $x=1.7$). In the case of C_2S, per mole of this clinker phase, 1–2 mol of CH are produced instead of $(2-H/S)$, in the case of C_3S, per mole of this clinker phase, 2–3 mol of CH are produced instead of $(3-H/S)$. Consequently, the condition in regard to sufficient CH production for the formation of C_4AH_{22} and $C_4A\bar{C}_{0.5}H_{12}$, as given in the previous Section (Eqs. (50) and (51)), will therefore also be valid in case part of the C_2S and/or C_3S reacts with C_4AF to from hydrogarnet and/or gehlenite hydrate.

4.3. Compressed water

By using Eqs. (55) and (56), the molar volumes listed in Table 1 and setting $x=2$, the density of the water can be assessed that is retained in P-dried state. Subtracting the molar volumes of the reactants from the reaction products appearing in Eq. (55) yields 117.21 cm^3 shrinkage per mole of reacted C_4AF. This reaction involves 10 moles of water (to form 1 $C_6AFS_2H_8$ and 2 CH), with the molar density of water (Table 1) it follows that $v_n=0.65$ cm^3/g, which is 10% smaller than the density of the non-evaporable water involved with the C_2S reaction that results in C–S–H and CH and the overall value measured by Powers and Brownyard [1], namely $v_n=0.72$ cm^3/g ([2–4]). For the reaction of C_4AF with C_3S (Eq. (56)), a similar computation reveals a shrinkage of the solids of 140.43 cm^3 per mole reacted C_4AF, as 12 moles water are involved (to form 1 $C_6AFS_2H_8$ and 4 CH), again $v_n=0.65$ cm^3/g is obtained. In supersaturated state, it is most likely that the extra "gel" water, i.e., the extra retained water (10 H), by the hydrogarnet is not compressed (specific molar volume: 18.02 cm^3/mol). The resulting molar volume and density of $C_6AFS_2H_{18}$ are included in Table 1.

The average v_d for the C_2S and C_4AF reaction therefore amounts 0.83 cm^3/g (=0.5 *x* (0.65 cm^3/g+1 cm^3/g)), and for the C_3S and C_4AF reaction it amounts 0.84 cm^3/g (=(10 × 0.65 cm^3/g+12 × 1 cm^3/g)/22). Using the same computation scheme and invoking $v_n=0.72$ cm^3/g and $v_g=0.90$ cm^3/g, the average values become 0.81 cm^3/g for a both reactions. In other words, the specific densities encountered in the previous section and in Ref. [2], viz. $v_n=0.72$ cm^3/g and $v_g=0.90$ cm^3/g, serve well to describe the formation of supersaturated hydrogarnet. The specific density of the non-evaporable water is overestimated, and of the gel water underestimated, but the average agrees well. This approach enables the use of general values of v_n (0.72 cm^3/g) and v_g (0.90 cm^3/g), which are applicable to all reactions of the five clinker phases considered.

Though considered as not likely, when gehlenite hydrate is formed, Eqs. (65) and (66) need to be considered and hence, the molar volume of the Fe containing gehlenite hydrate needs to be assessed. By comparing the molar volumes of C_6AFH_{12} and C_3AH_6 it follows that the replacement of Al by Fe causes an increase of 5.35 cm^3/mole per mole of C_6AFH_{12}. Applying this volume increase by Fe substitution to the molar volume of C_2ASH_8, results in the molar volume of $C_4AFS_2H_{16}$ (and its pertaining density) that is included in Table 1. Subsequently, comparing the solids volume in Eqs. (65) and (66) yields a mean molar water volume of 16.79 cm^3/mol ($v_d=0.93$ cm^3/g) and 16.32 cm^3/mol ($v_d=0.91$ cm^3/g), respectively. This water is partly non-evaporable (10/20 and 12/22 for C_2S and C_3S, respectively) and partly gel water (10/20 for both C_2S and C_3S, respectively). Using $v_n=0.72$ cm^3/g and $v_g=0.9$ cm^3/g, as average $v_d=0.81$ cm^3/g and $v_d=0.80$ cm^3/g is obtained for reactions (65) and (66), respectively. This is matching poorly with $v_d=0.93$ cm^3/g and $v_d=0.91$ cm^3/g (as computed above). On the other hand, using $v_n=0.72$ cm^3/g and $v_g=1.1$ cm^3/g, as average $v_d=0.91$ cm^3/g and $v_d=0.89$ cm^3/g is obtained for Eqs. (65) and (66), respectively. These values are in better agreement with the previously determined values based on the reaction scheme. This implies that the gel water involved with the formation of gehlenite is expanded (or the non-evaporable water less compressed).

5. Conclusions

Powers and Brownyard (1947) [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 non-evaporable water and gel water. The water retention in P-dried and saturated states was furthermore related to the clinker composition of the cement. The most important features of the model were discussed in detail in Part I [2], and the model was furthermore applied to the individual reactions of alite and belite. In this paper, their water retention data are applied to the individual reactions of the aluminate, ferrite and calcium sulphate phases. This application, making use of water retention in P-dried and saturated state, gives quantitative information on the hydration products formed (after 126 days and longer).

From the present analysis it follows that the ferrite phase reacts with the calcium silicates to form a supersaturated hydrogarnet ($C_6AFS_2H_{18}$) and CH. The remaining calcium silicates react to form $C_{1.7}SH_{3.2}$ and CH [2–4]. This reaction mechanism of the ferrite phase implies that in the presence of ferrite less C–S–H and more CH are formed than without ferrite. It furthermore seems that the aluminate exclusively reacts with the calcium sulphate phase, to form tetra calcium aluminate hydrate, ettringite, hemi-carbonate and mono-sulphate. The quantities of these products can be specified when the degree of carbonation of the mono-sulphate, α, is known. Here, it is assumed that during the experiments of Powers and Brownyard [1], the mono-sulphate was fully carbonated, and based on this expressions for the four hydration products derived for any given α: Eqs. (36) and (40)–(42). These molar quantities have been specified at RH=100% and an age of about 1 year, but can be assumed to be applicable at lower RH and at older ages as well. From the analysis one can readily see the effect of sulphate on the products formed, and how little carbonate in the cement is actually needed for full carbonation of the mono-sulphate.

The reactions and reaction products can also be used to validate the magnitude of two important properties of the model of Powers and Brownyard [1], viz. the specific volume of non-evaporable water (v_n) and of gel water (v_g) are specified. 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 present reaction equations and products, as well as the results from [2], it follows that $v_n = 0.72$ cm^3/g and $v_g = 0.90$ cm^3/g are appropriate for all clinker phases reactions.

There are some limitations of the analysis presented here. For instance the formation of hydrocalcite from MgO is not considered, as the five major clinker phases are studied only. For cements with low MgO content this omit introduces a small error. Moreover, the reaction and composition of mature pastes is considered only. By introducing a degree of hydration and a degree of carbonation in time (which may have different time scales), a quasi-transient reaction model could however be obtained. Such a model could also allow for the reduction of water retention by the C–S–H in time, as discussed in [2]. Summarizing, it is believed that the present analysis not only contributes to clarification of the model and experiments by Powers and Brownyard [1], but that it will also facilitate future engineering with Portland cement and products derived there from.

List of Symbols

Roman

A	Al_2O_3
B	$=B' + 1 = (w_g + w_n)/w_n$
B'	w_g/w_n
c	Mass of reacted cement [g]
C	CaO
$\bar{C}$	CO_2
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
$C\bar{S}H_{0.5}$	Hemi-hydrate
$C\bar{S}H_2$	Gypsum
C_4AF	Ferrite or pure C_4AF
F	Fe_2O_3
H	H_2O
k	Number of absorbed layers of gel water
M	Mass of one mole of substance [g/mol]
m	Mass of reacted phase or formed product [g]
n	Number of moles
RH	Relative humidity
S	SiO_2
$\bar{S}$	SO_3
V	Volume [cm^3]
V_m	Mass of water in first absorbed layer [g]
w	Mass of reacted water [g]
x	Mass fraction

Greek

α	Degree of carbonation of mono-sulphate phase
v	Specific volume [cm^3/g]
ρ	Density [g/cm^3]
ω	Specific molar volume [cm^3/mole]

Subscript

c	Cement
d	Compressed water (gel water + non-evaporable water)
g	Gel
hc	Hydrated cement
hp	Hydration product ("gel")
n	Non-evaporable
s	Shrinkage
w	Capillary water
x, y	Molar ratios in chemical formulas

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Appendix A

The analysis in Section 3 is based on the assumption that during the experiments of Powers and Brownyard [1] all mono-sulphate has been converted into hemi-carbonate (and/or mono-carbonate). In this Appendix the line is followed that no carbonation has occurred, i.e., their experiments were perfectly CO_2-free. In that case, Eq. (32)–(35) hold again, with $\alpha = 0$ yielding

$$n_{C_4AH_{22}^0} = n_{C_3A} - \frac{1}{2} n_{C\bar{S}} \ , \tag{A.1}$$

$$n_{C_4A\bar{S}H_{14}^0} = \frac{1}{4} n_{C\bar{S}} \ , \tag{A.2}$$

$$n_{C_6A\bar{S}_3H_{36}^0} = \frac{1}{4} n_{C\bar{S}} \ , \tag{A.3}$$

and obviously $n_{C_4A\bar{C}_{0.5}H_{12}^0} = 0$, of course. To obtain the quantities in a fully carbonated system, Eqs. (28) and (29) yield

$$n_{C_4A\bar{C}_{0.5}H_{12}^1} = \frac{1}{6} n_{C\bar{S}} \ , \tag{A.4}$$

$$n_{C_6A\bar{S}_3H_{36}^1} = \frac{1}{3} n_{C\bar{S}} \ , \tag{A.5}$$

and $n_{C_4A\bar{S}H_{14}} = 0$ now. Eq. (A.1) also prevails for this case (i.e., $n_{C_4AH_{22}^1} = n_{C_4AH_{22}^0}$) as carbonation is only changes amount of ettringite, mono-sulphate and hemi-carbonate via Eq. (26).

For the full carbonation of mono-sulphate, $n_{C\bar{C}}/n_{C\bar{S}}$ apparently needs to be 1/12 (see Eq. (A.4)), or $m_{C\bar{C}}/m_{C\bar{S}}=6\%$ (molar masses taken from Table 1). So, related to the mass of anhydrite, only 6% of calcite is required for full carbonation.

For an arbitrary degree of carbonation, Eqs. (A.2), (A.3) and (27) (28) (29) yield

$$n_{C_4A\bar{S}H_{14}} = \frac{1}{4}(1-\alpha)n_{C\bar{S}} \ , \tag{A.6}$$

$$n_{C_4A\bar{C}_{0.5}H_{12}} = \frac{1}{6}\alpha n_{C\bar{S}} \ , \tag{A.7}$$

$$n_{C_6A\bar{S}_3H_{36}} = \frac{1}{12}(3+\alpha)n_{C\bar{S}} \ . \tag{A.8}$$

For all α, the amount of C_4AH_{22} follows from Eq. (A.1). From these equations one can compute the water retention at arbitrary carbonation. Considering the water retention of each substance and their quantity (expressed in n_{C_3A} and $n_{C\bar{S}}$) yields

$$n_{H,d} = 21\ n_{C_3A} + \left(2+\frac{17\alpha}{12}\right)n_{C\bar{S}} \ . \tag{A.9}$$

From this equation it follows that indeed the coefficient pertaining to $n_{C\bar{S}}$ takes a value of 2 when there is no carbonation (as fitted, Eq. (11). When carbonation occurs, the water retention is increased as by conversion of mono-sulphate to hemi-carbonate and ettringite effectively more water is retained, see Eq. (26).

From Eqs. (A.6)-(A.8) the following quantitative results conclusions follow. The moles of mono-sulphate, hemi-carbonate (plus possible mono-carbonate) and ettringite formed only depend on $n_{C\bar{S}}$, but their ratio being constant and depending on the degree of carbonation only:

$$\frac{n_{C_4A\bar{C}_{0.5}H_{12}}}{n_{C_6A\bar{S}_3H_{36}}} = \frac{2\alpha}{3+\alpha} \ , \tag{A.10}$$

$$\frac{n_{C_4A\bar{S}H_{14}}}{n_{C_6A\bar{S}_3H_{36}}} = \frac{3(1-\alpha)}{3+\alpha} \ . \tag{A.11}$$

For full carbonation of the mono-sulphate ($\alpha=1$), the moles of hemi-carbonate is half the amount of moles of ettringite formed. In a CO_2-free environment (laboratory conditions, $\alpha=0$, here assumed to prevail during the experiments by Powers and Brownyard [1], the moles of ettringite and mono-sulphate formed are equal.

The mass ratios can be computed by using the molar masses from Table 1:

$$\frac{m_{C_4A\bar{C}_{0.5}H_{12}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \frac{\alpha}{3+\alpha} \ , \tag{A.12}$$

$$\frac{m_{C_4A\bar{S}H_{14}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \frac{3(1-\alpha)}{2(3+\alpha)} \ , \tag{A.13}$$

respectively. Hence, in a fully carbonated the system the mass ratio of ettringite to hemi-carbonate is about 4, and in CO_2-free system the mass ratio of ettringite to mono-sulphate is about 2.

The hemi-carbonate and mono-sulphate formed can be expressed in amount of ettringite formed, as this latter product is always formed. The ratios appear not to depend on n_{C_3A} nor $n_{C\bar{S}}$. It is interesting now to determine the ratio of tetra calcium aluminate hydrate formed to ettringite formed. Combining Eqs. (A.1) and (A.8) yields:

$$\frac{n_{C_4AH_{22}}}{n_{C_6A\bar{S}_3H_{36}}} = \left[\frac{12}{3+\alpha}\right]\left[\frac{n_{C_3A}}{n_{C\bar{S}}} - \frac{1}{2}\right] . \tag{A.14}$$

One can readily see that the first factor on the right-hand side takes value of three for the carbonated system and four for the CO_2-free system, respectively. Using the molar masses listed in Table 1, this equation can be expressed as

$$\frac{m_{C_4AH_{22}}}{m_{C_6A\bar{S}_3H_{36}}} \approx \left[\frac{3}{3+\alpha}\right]\left[\frac{x_{C_3A}}{x_{C\bar{S}}} - 1\right] \tag{A.15}$$

Apparently, irrespective the degree of carbonation, to bind all sulphate (i.e., so that no aluminate hydrate is formed), the number of moles C_3A (n_{C_3A}) needs to be half the number of moles of $C\bar{S}$ ($n_{C\bar{S}}$). This corresponds to a mass ratio $m_{C\bar{S}}/m_{C_3A}$ in the cement (or $x_{C\bar{S}}/x_{C_3A}$) of unity. If all sulphate were added as gypsum, in Eq. (A.15) $x_{C\bar{S}}$ needs to be replaced by $0.8x_{C\bar{S}H_2}$.

The computed minimum value for $n_{C_3A}/n_{C\bar{S}}$ (=1/2) is larger than the value that one would expect if all C_3A would be converted into ettringite, namely 1/3. This is due to the fact that mono-carbonate is formed simultaneously in a carbonating environment, which is also binding C_3A. Also in a CO_2-free environment the amount of moles C_3A (n_{C_3A}) needs to be half the moles of $C\bar{S}$ ($n_{C\bar{S}}$). This value is owing to the fact that besides ettringite also mono-sulphate prevails, which binds only one mole of $C\bar{S}$ per mole of C_3A.

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