



Alkali concentrations of pore solution in hydrating OPC

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Abstract

In order to study the pore solution, the release and binding of alkalis in a hydrating cement system have been studied. First, the binding factors for sodium and potassium as determined by Taylor [Adv. Cem. Res. 1 (1987) 5] and the corresponding distribution ratios as determined by Hong and Glasser [Cem. Concr. Res. 29 (1999) 1893; Cem. Concr. Res. in press] are related to each other. It follows that the sorption of sodium is practically identical, whereas for potassium Taylor [Adv. Cem. Res. 1 (1987) 5] predicts a substantial lower degree of sorption. The concept of alkali release, pore solution decrease and sorption by formed calcium-silicate hydrate (C-S-H), is incorporated in the NIST hydration model (CEMHYD3D). Subsequently, the model is compared with ordinary Portland cement (OPC) hydration experiments reported by Larbi et al. [Cem. Concr. Res. 20 (1990) 506]. Good agreement is obtained when the distribution ratios of Hong and Glasser [Cem. Concr. Res. 29 (1999) 1893] are applied. The results suggest that C-S-H is the only binder of alkalis in hydrating OPC.

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1. Introduction

In a hydrating cement paste, concentrations of pore solution change continuously [1]. Knowing the concentration of ions is important for many reasons. For instance, the hydroxyl concentration and related pH are important parameters that determine the reactivity of cement additives. Fraay et al. [2] mentioned a threshold pH that was required for the reaction of fly ash. Song and Jennings [3] and Brouwers and van Eijk [4] studied the effect of pH on the alkali activation of slags and fly ash, respectively. Also, the likelihood of the undesired alkalis–silica reaction in concrete is greatly affected by the hydroxyl concentration and pH of the pore solution [5].

Cement is also used as a binder in solidification/stabilization (S/S) processes for treating wastes. These wastes often precipitate as insoluble salts and may form an impermeable layer around the cement grains and thus inhibit further hydration reactions. Solubility and precipitation of these compounds obviously depend on hydroxyl concentrations, which is the second motivation for determining the

pH of the pore solution. In order to describe the effects of the presence of these ions during cement hydration, the relevant chemical equilibria should be taken into account. The first step in determining the pore solution composition is the computation of the alkali concentration (van Eijk [6]).

In this paper, the method of Taylor [5] that describes the release of alkalis from cement and alkali sorption by the hydration products is used. The work on sorption by the calcium-silicate hydrate (C-S-H) phase by Hong and Glasser [7,8] will also be employed. The binding factors given by these authors are compared and related to each other. Subsequently, the theory on alkali release and sorption by C-S-H is incorporated in the numerical hydration model, CEMHYD3D, as developed by the NIST [9]. Finally, the alkali concentration as predicted by the model is compared with measured values during ordinary Portland cement (OPC) hydration experiments reported by Larbi et al. [13].

2. Binding model

Both Taylor [5] and Hong and Glasser [7,8] have reported binding factors for alkalis. In both publications, equilibrium was assumed between (pore) water and reaction products. Taylor [5] based the binding factors on all the reaction products formed. As sorption mainly takes place in

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the reaction product, C-S-H, Hong and Glasser [7,8] measured the partition of potassium and sodium in a solution and C-S-H of various Ca/Si molar ratios. They concluded that steady state was attained within 2–3 days. Their alkali hydroxide concentrations (NaOH and KOH) ranged from 1 to 300 mM. Based on the attained equilibrium between solution and C-S-H, distribution ratios R_d were computed. In this section, two binding models will be discussed, and the binding factors of Taylor [5] will be related to and compared with the distribution ratios of Hong and Glasser [7].

Taylor [5] developed a method to describe the alkali content in cement pore solution. It is based on the total alkali content in cement, the w/c ratio used and the hydration degree. When the release and uptake of alkalis in reaction products and the porosity fraction are known, the concentration of alkalis and corresponding $[\text{OH}^-]$ can be predicted during hydration. All properties were based on 100 g of anhydrous cement.

The total numbers of moles of Na^+ and K^+ present per mass of cement were calculated from the corresponding mass fractions and molecular masses. For Na the calculation is as follows:

$$\text{Na}_T = \frac{2f_{\text{Na}_2\text{O}}}{M_{\text{Na}_2\text{O}}} \quad (1)$$

where Na_T = total Na content (mol/g); $f_{\text{Na}_2\text{O}}$ = Na_2O mass fraction (g/g); $M_{\text{Na}_2\text{O}}$ = molar mass of Na_2O (g/mol).

Alkalis in cement are partly present as readily soluble sulphates and partly bound in the major clinker minerals [5]. The alkalis present as sulphate will dissolve rapidly and will be in solution before hydration of silicates takes place. The remaining fractions of alkalis are released during hydration. The distribution of alkalis and SO_3 in clinkers with different amounts of alkalis and sulphates can among others be found in Taylor [1] and Pollitt and Brown [10]. The amount of Na^+ released rapidly is calculated as follows:

$$\text{Na}_{\text{sulphate}}^+ = f_{\text{Na,sulphate}} \text{Na}_T \quad (2)$$

where $\text{Na}_{\text{sulphate}}^+$ = Na^+ released from sulphates (mol/g); $f_{\text{Na,sulphate}}$ = fraction of Na present as sulphate.

It is assumed that the alkalis bound in the major clinker minerals are evenly distributed over the major clinker phases, and will be released into the pore solution as soon as the clinker reacts and dissolves. The amount of Na^+ released from the clinker is thus linearly proportional to the hydration degree:

$$\text{Na}_{\text{hydroxide}}^+ = f_{\text{Na,hydroxide}} \text{Na}_T \alpha \quad (3)$$

where $\text{Na}_{\text{hydroxide}}^+$ = Na^+ released from clinker (mol/g); α = hydration degree.

Note that $f_{\text{Na,hydroxide}} + f_{\text{Na,sulphate}} = 1$. It is assumed that all porosity is completely filled with pore solution (i.e. hardening takes place under saturated condition, the volume change by chemical shrinkage is filled with external water)

and equals the amount of free water present in the system that also contains all ions of interest. The total number of moles of Na released per mass of cement and before any uptake by pore solution and reaction products is the sum of Na released from sulphates and from clinker minerals. This sum is:

$$\text{Na}_{\text{released}}^+ = \text{Na}_{\text{sulphate}}^+ + \text{Na}_{\text{hydroxide}}^+ \quad (4)$$

Taylor [5] discusses that the amount of each alkali cation taken up by the hydration products (C-S-H and AFm) is proportional to the concentration present in the solution and the quantity of these hydration products formed, thus:

$$\text{Na}_{\text{released}}^+ m_{\text{OPC}} = [\text{Na}^+] V_w + b_{\text{Na}} [\text{Na}^+] \alpha \quad (5)$$

where m_{OPC} = mass of ordinary Portland cement (g); V_w = volume of water (cm^3); $[\text{Na}^+] = \text{Na}^+$ concentration in pore solution (mol/cm^3); b_{Na} = binding factor Na^+ (cm^3).

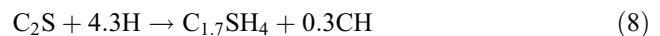
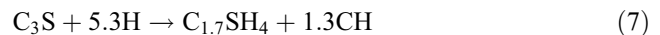
The first factor on the right-hand side accounts for the dissolved sodium ion in the pore solution, whereas the second term accounts for the adsorbed ions, which is proportional to the concentration in the pore solution and amount of formed reaction product, i.e. α .

Hong and Glasser [7,8] mention C-S-H contribute most to the apparent sorption, as it is a good sorbent and the most abundant reaction product. Employing their concept of binding yields

$$\text{Na}_{\text{released}}^+ m_{\text{OPC}} = [\text{Na}^+] V_w + R_d [\text{Na}^+] m_{\text{C-S-H}} \quad (6)$$

where R_d = distribution ratio (cm^3/g); $m_{\text{C-S-H}}$ = mass of formed C-S-H (g).

To relate the binding factor b_{Na} to the distribution ratio R_d , the mass of C-S-H formed has to be related to the amount of cement reacted. In OPC, C-S-H is overwhelmingly formed from the hydration reaction of the major clinker minerals C_2S and C_3S , following Bentz [9]:



Considering that the OPC of Taylor [5] consisted of 60% (m/m) C_3S and 15% (m/m) C_2S , and that the molecular masses of C_2S , C_3S and $\text{C}_{1.7}\text{SH}_4$ are 172, 228 and 229 g/mol [9], respectively, and using Eqs. (7) and (8), it follows that

$$m_{\text{C-S-H}} = 0.8\alpha m_{\text{OPC}} \quad (9)$$

Now we are in a position to relate b_{Na} (Eq. (5)) to R_d (Eq. (6)):

$$R_d = \frac{b_{\text{Na}}}{0.8m_{\text{OPC}}} \quad (10)$$

Taylor's [5] values of b_{Na} and b_{K} , 31 and 20 cm^3 , respectively, were based on 100 g OPC. Substituting these values into Eq. (10) yields the corresponding R_d for sodium

Table 1
Distribution ratios (cm^3/g)

	Taylor [5]	Hong and Glasser [7]
Na^+	0.39	0.39
K^+	0.25	0.38

and potassium, which are included in Table 1. This table also includes R_d , as measured by Hong and Glasser [7], the values pertaining to $C/S=1.8$ and 300 mM/l (range of interest).

From this table it follows that Taylor [5] and Hong and Glasser [7] found the same distribution ratio for sodium. This finding suggests that indeed all sodium binding in hydrating OPC can be attributed to C-S-H. Furthermore, one can see the major difference in R_d for potassium. Taylor [5] found a bigger difference between binding of sodium and potassium than Hong and Glasser [7]. In the next section, the theory on binding is incorporated into a numerical hydration model and compared with experiments.

3. Computations and comparison with experiments

The sorption model can be incorporated into the NIST hydration model, CEMHYD3D, which is described in detail by Bentz [9]. The model simulates the reactions between cement clinker minerals and water. It starts with a digitised matrix of pixels with a unit size of $1 \mu\text{m}^3$, which are assigned to water, gypsum or one of the cement mineral phases. A simulation consist of dissolution cycles in which solid phases are scanned and can dissolve, react, diffuse and precipitate as $\text{Ca}(\text{OH})_2$, (CH) or C-S-H. After each hydration cycle, it predicts the hydration degree, the porosity and the phase composition of the microstructure at that stage. The model has been very successful in predicting temperature rises [11] and for investigating relations between particle size distribution (PSD), w/c ratio and hydration degree [12].

The model on binding, as described in the previous section, has been incorporated into this model. It is assumed that the binding of the alkalis is fully caused by C-S-H; accordingly, Eq. (6) is used as this equation accounts for the actual amount of C-S-H formed. For cements that contain other amounts of C_2S and C_3S than the cement on which Taylor [5] based his binding factors [15% (m/m) C_2S and 60% (m/m) C_3S], his binding factors are not applicable. Finally, the numerical prediction will be compared with experiments reported by Larbi et al. [13].

Larbi et al. [13] determined pore solution concentrations in pastes prepared with an OPC having a PSD and a mineral composition that closely corresponds to ENCI CEM I 32,5 R cement (Blaine surface $286 \text{ m}^2/\text{kg}$ [6]). The composition of the “Larbi” cement and CEM I 32,5 R cement is given in Table 2, panels a and b, respectively. As the mineral composition and PSD are quite similar, and CEMHYD3D

has been calibrated for CEM I 32,5 R [6], this latter cement is used for the computations. However, the values of the “Larbi” cement for alkali have been used (Table 2a), as well as the appropriate w/c ratio of 0.45. Curing took place at a temperature of 20°C . The pore solution was obtained at different points in time using a pore fluid expression apparatus similar to that used by Longuet et al. [14]; $[\text{Na}^+]$ and $[\text{K}^+]$ in the extracted pore solution were determined using flame emission spectroscopy.

CEMHYD3D simulations were executed using the discretised PSD of CEM I 32,5 R, its mineral composition (Table 2b), water saturated conditions, and w/c ratio and temperature corresponding to experimental conditions. van Eijk [6] calibrated the model for CEM I 32,5 R and CEM I 52,5 R cements using both chemical shrinkage and calorimetric measurements. The alkali fractions are given in Table 2a. To assess the distribution between alkalis that dissolve rapidly and are released during hydration, the molar ratio $[\text{SO}_3]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}])$ of the clinker minerals needs to be known [1]. The SO_3 mass fraction listed in Table 2a comprises the total of SO_3 stemming from both clinker minerals and gypsum. From Blaakmeer [15], it follows that

Table 2

a. Oxide composition of cement used for pore solution determination [13]

Oxide	Mass (%)
CaO	61.90
SiO_2	19.94
Al_2O_3	5.57
Fe_2O_3	2.91
K_2O	0.82
Na_2O	0.21
SO_3	3.10
MgO	1.50

b. Oxide composition of cement (CEM I) used for computation and pertaining mineral composition of cement clinker using modified Bogue method [1]

Oxide	Mass (%)
CaO	64.40
SiO_2	20.36
Al_2O_3	4.96
Fe_2O_3	3.17
K_2O	0.64
Na_2O	0.14
SO_3	2.57
MgO	2.09
TiO_2	0.35
Mn_3O_4	0.14
P_2O_5	0.18
LOI	0.88

Mineral

C_3S	61
C_2S	15
C_3A	6
C_4AF	10

Table 3

Source	Release	Na ⁺	K ⁺
<i>a. Fractions of Na and K present in sulphates or clinker minerals in ENCI cements as taken from Taylor [1] and Pollitt and Brown [10]</i>			
Alkali sulphates	Rapidly	0.45	0.90
Clinker minerals	During hydration	0.55	0.10
<i>b. Fractions of Na and K present in sulphates or clinker minerals in ENCI cements as fitted</i>			
Alkali sulphates	Rapidly	0.35	0.55
Clinker minerals	During hydration	0.65	0.45

the clinker minerals contain about 0.8–1.0% (mass) SO₃, and a mean value of 0.9% is used henceforth. Using the molar masses of SO₃ (80.1 g/mol), Na₂O (62 g/mol) and K₂O (94.2 g/mol), it follows that [SO₃]/([Na₂O]+[K₂O])=0.93 for the “Larbi” cement. From Taylor [1], it follows that 45% and 90% of Na and K, respectively, are present as readily soluble sulphates. Table 3a summarises these values.

As distribution ratios, the values of Table 1 were used for the computations, which were executed with the values of Taylor [5] and Hong and Glasser [7]. Table 4a gives the results for computations of alkali concentrations using CEMHYD3D. As the model has been calibrated for CEM I 32,5 R [6], cycles could be related to real time. The amounts released are included in this table, defined as

$$[\text{Na}^+]_{\text{max}} = \frac{m_{\text{OPC}} \text{Na}^+_{\text{released}}}{V_w} \quad (11)$$

whereby Na⁺_{released} follows from Eq. (4). Note that [Na⁺]_{max} represents the actual pore solution concentration assuming there would be no sorption of alkalis by the

reaction products formed. Furthermore, a concentration factor is included, giving:

$$\frac{\varphi_p}{\varphi_p^0} = \frac{V_w}{V_0} \quad (12)$$

where V₀=initial volume of water (cm³).

This accounts for the reduction in the actual pore solution volume during hydration as water is bound in reaction products, and reads

$$V_w = V_0 - V_b \quad (13)$$

where V_b=bound water (cm³).

The concentration factor readily follows from dividing the number of current water pixels by the initial number of water pixels. In Table 4a, the concentrations of Na⁺ and K⁺ according to the R_d values of Taylor [5] and Hong and Glasser [7] are listed, using the values in Table 1. To apply the model of Hong and Glasser [7], one needs to determine the mass of C-S-H. This follows by multiplying the volume (number of pixels) of C-S-H by its density, 2.12 g/cm³ [9].

One can see that the prediction for [Na⁺] is identical when using the models of Taylor or of Hong and Glasser. This would be expected, as the values for R_d are the same (Table 1). On the other hand, the prediction of [K⁺] is different, as the values for R_d differ. The value of Taylor [5] is lower, resulting in less binding of K⁺ and a higher concentration of this ion in the pore solution. Table 4 also reveals that, depending on the values for R_d used, after 28 days about 50% to 60% of the released alkali ions are adsorbed. This implies that the binding of the alkalis is indeed a major effect that should be taken into account when studying the pore solution composition.

Table 4

Time (days)	α	ϕ _p /ϕ _p ⁰	[Na ⁺] _{max}	[Na ⁺] _{Taylor}	[Na ⁺] _{H&G}	[Na ⁺] _{meas}	[K ⁺] _{max}	[K ⁺] _{Taylor}	[K ⁺] _{H&G}	[K ⁺] _{meas}
<i>a. Calculated and measured pore solution concentrations, based on values in Table 3a</i>										
0.25	0	1.00	0.07	0.07	0.07	0.05	0.35	0.35	0.35	0.21
0.50	0.21	0.80	0.10	0.09	0.09	0.05	0.45	0.40	0.38	0.23
1	0.30	0.72	0.12	0.10	0.10	0.05	0.50	0.42	0.39	0.24
2	0.38	0.66	0.15	0.11	0.11	0.06	0.55	0.43	0.39	0.26
3	0.43	0.63	0.17	0.11	0.11	0.07	0.58	0.44	0.39	0.26
7	0.53	0.56	0.20	0.12	0.12	0.11	0.66	0.45	0.39	0.33
14	0.61	0.51	0.23	0.12	0.12	0.13	0.73	0.46	0.40	0.36
28	0.68	0.46	0.27	0.13	0.13	0.14	0.82	0.48	0.40	0.37
<i>b. Calculated and measured pore solution concentrations, based on values in Table 3b</i>										
0.25	0	1.00	0.05	0.05	0.05	0.05	0.21	0.21	0.21	0.21
0.50	0.21	0.80	0.10	0.08	0.08	0.05	0.32	0.28	0.27	0.23
1	0.30	0.72	0.11	0.09	0.09	0.05	0.37	0.31	0.29	0.24
2	0.38	0.66	0.14	0.10	0.10	0.06	0.42	0.33	0.30	0.26
3	0.43	0.63	0.15	0.10	0.10	0.07	0.46	0.34	0.31	0.26
7	0.53	0.56	0.18	0.11	0.11	0.11	0.54	0.37	0.33	0.33
14	0.61	0.51	0.22	0.12	0.12	0.13	0.63	0.40	0.34	0.36
28	0.68	0.46	0.25	0.13	0.13	0.14	0.72	0.42	0.35	0.37

“Taylor” refers to used values of Taylor (Table 1), “H&G” refers to used values of Hong and Glasser (Table 1), “meas” refers to measured pore solution concentrations [13]. Concentrations are in mol/l.

Table 4a also lists the results of the corresponding pore solution measurements by Larbi et al. [13]. The agreement between computed and measured $[\text{Na}^+]$ and $[\text{K}^+]$ is good for mature paste, after 28 days. It also follows that $[\text{K}^+]$ is better predicted when the value of Hong and Glasser [7] is used for the binding of this ion. However, in general, one can see that at early ages the model yields an alkali release that is too high. Taylor [1] already mentions that the experimental conditions of Pollitt and Brown [10] do not necessarily correspond to the conditions met during hydration. Accordingly, the computations have also been executed with a modified distribution of the alkalis in sulphate and in clinker minerals (Table 3b) (i.e. less alkalis as sulphate). In Table 4b, the computational results pertaining to Table 3b are summarized. The slower alkali release now results in good agreement between experiments and model also at early ages. Again, the agreement for $[\text{K}^+]$ is best when the binding value of Hong and Glasser [7] is used. Table 4a and b reveals that for the first 2 to 3 days, the measured alkali concentrations are lower than computed. In other words, one can say they lag behind. Hong and Glasser [7,8] noticed that equilibrium is attained after 2 to 3 days, whereas the model starts from equilibrium. The difference between measured and computed values may therefore stem from the absence of equilibrium the first days. In such case, the alkalis would first be incorporated in the reaction products, and released to the pore solution thereafter. More likely, the discrepancy could be caused by the assumption of alkalis evenly distributed over the major clinker phases. Based on X-ray analysis, Taylor [5] found that the alite, belite, aluminate and ferrite phases all have different contents of alkalis. Each phase is having a different reaction rate (also in CEMHYD3D), so that the release is not directly proportional to the overall hydration degree α . For larger α , the error involved clearly becomes smaller, as then most alkalis are released, regardless which phases were containing them.

Summarizing, the binding model and resulting equation (Eq. (6)) is useful to describe release, pore solution reduction (concentration) and sorption of alkalis in OPC. CEMHYD3D can be used to give the degree of hydration and the amount of unbound water as a function of time. For each of the two alkali ions, only the following parameters have to be known: the amount of alkalis, the fraction present as alkali sulphate and the distribution ratios/binding factors. The distribution of the alkalis is particularly important at early ages. The distribution ratio is of great importance at all ages and hence, is needed for the prediction of the alkali concentration in mature paste, which is most important. Furthermore, the simplification of evenly distributed alkalis over the major clinker is also more correct at larger ages.

4. Conclusions

Determining the alkali concentration is the first step in the understanding of the pore solution composition in a

hydrating water–cement mixture. The binding factor and distribution ratios of Taylor [5] and Hong and Glasser [7,8], respectively, can be related to each other (Eq. (10)) and compared (Table 1). It follows that the distribution ratios for sodium are practically identical and that for potassium they are different. According to Hong and Glasser [7,8], the distribution ratios of sodium and potassium are nearly equal, whereas Taylor [5] finds a much smaller binding factor for potassium, for which there is not yet an explication. As the binding factor of Taylor [5] is based on all the hydration products, and the distribution ratio of Hong and Glasser [7,8] on C-S-H, the agreement between the values for sodium suggests binding by the C-S-H phase only.

Subsequently, the theory on sorption (binding/distribution) is incorporated into a model of Portland cement hydration (CEMHYD3D). This model was used to describe hydration degree, alkali release, C-S-H formation and decrease in amount of pore solution as a function of time. From these parameters, the alkali content of the cement and the alkali sorption model, the concentrations of alkalis in OPC pore solution were calculated.

The observed trends agreed very well with experimental results reported by Larbi et al. [13] when the binding factors/distribution ratios of Hong and Glasser [7] are used. It also seems that the sulphate content as proposed by Taylor [1] and Pollitt and Brown [10] is too high, with a lower content of alkalis as sulphates, thus better agreement is obtained. The results support the idea that the C-S-H phase may be the only alkali-binding phase. Furthermore, the results could also imply that during the first days equilibrium is not prevailing (which is also supported by the findings of Hong and Glasser [7,8]). In that case, the alkalis are first present in the reaction products, and subsequently released there from, for which few days are needed. More likely, the discrepancy could be caused by the assumption of alkalis evenly distributed over the major clinker phases, which is not the case in reality. Accordingly, the release is not directly proportional to the overall hydration degree α , as is assumed by CEMHYD3D. On the other hand, for large α , the error involved clearly becomes smaller, as then most alkalis are released, regardless which phases were containing them. Concluding, the presented method and pertaining parameters appear to be a useful tool for future computations of the pore solution composition in hydrating OPC, especially at higher hydration degrees.

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