



Alkali binding in hydrated Portland cement paste

W. Chen^{a,b,*}, H.J.H. Brouwers^c

^a Key Laboratory of Silicate Materials Science and Engineering of Ministry of Education, Luoshi road 122, 430070, Wuhan, PR China

^b School of Materials Science and Engineering, Wuhan University of Technology, Luoshi Road 122, 430070, Wuhan, PR China

^c Department of Architecture, Building and Planning, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

ARTICLE INFO

Article history:

Received 31 October 2006

Accepted 24 December 2009

Keywords:

Alkalis (D)
Hydration products (B)
Modeling (E)
Pore solution (B)
Portland cement (D)

ABSTRACT

The alkali-binding capacity of C–S–H in hydrated Portland cement pastes is addressed in this study. The amount of bound alkalis in C–S–H is computed based on the alkali partition theories firstly proposed by Taylor (1987) and later further developed by Brouwers and Van Eijk (2003). Experimental data reported in literatures concerning thirteen different recipes are analyzed and used as references. A three-dimensional computer-based cement hydration model (CEMHYD3D) is used to simulate the hydration of Portland cement pastes. These model predictions are used as inputs for deriving the alkali-binding capacity of the hydration product C–S–H in hydrated Portland cement pastes. It is found that the relation of Na^+ between the moles bound in C–S–H and its concentration in the pore solution is linear, while the binding of K^+ in C–S–H complies with the Freundlich isotherm. New models are proposed for determining the alkali-binding capacities of C–S–H in hydrated Portland cement paste. An updated method for predicting the alkali concentrations in the pore solution of hydrated Portland cement pastes is developed. It is also used to investigate the effects of various factors (such as the water to cement ratio, clinker composition and alkali types) on the alkali concentrations.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The hydration of cement is the reaction between the solid compounds and the liquid phase. The liquid phase contains some ions and is therefore called “pore solution”. The main types of ions in the pore solution are OH^- , K^+ , Na^+ , Ca^{2+} , SO_4^{2-} , $\text{Al}(\text{OH})_4^-$, H_3SiO_4^- , etc., with the alkali ions (K^+ and Na^+) and OH^- normally being the most dominant ones [6]. The hydroxyl concentration in the pore solution of concrete is important because it is one of the major factors on the likelihood of alkali-silica reaction (ASR), the immobilization of contaminants with cement, the alkaline environment around the steel bar to prevent its corrosion, and the reactivity of some supplementary materials (slag, fly ash etc.) in concrete. The number of researches on the alkali concentrations in the pore solution of hardening cement paste and concrete increased rapidly in the past decades. Effects of different factors were investigated. Most of the experimental analysis was based on the pore solution compression method firstly proposed by Longuet et al. [11].

Alkali ions are the most abundant cations in the solution and the charge is mainly balanced by the hydroxyl ions. Knowledge about the distribution of alkali ions in the solid phase and the solution is valuable for a better understanding of the development of the hydroxyl concentration in the pore solution of concrete. Efforts have

been made to investigate the partition of alkali ions [18] in the solids and in the solution. It is possible to simulate the development of alkali ion concentrations and in turn the hydroxyl concentration with some methods if the volume of the pore solution in concrete and the amount of alkali ions it contains are predicted [3,18]. Such methods may be used to investigate the effects of different factors on the hydroxyl concentration without the need of carrying out the time-consuming and costly compression experiments.

The amount of alkali ions taken up by the solid hydration products depends on their amounts as the result of cement hydration and the alkali-binding capacities of these products. The latter is more complex since the amounts of hydration products may be predicted with stoichiometric equations of cement hydration or with some computer models while the alkali-binding capacities of hydration products in hydrated Portland cement paste can hardly be measured directly. Therefore, researches on the alkali-binding capacities of hydration productions in hydrated Portland cement paste will help in developing methods for predicting the hydroxyl concentrations in the pore solution, and understanding the effects of different factors.

The alkali-binding capacity of the hydration product C–S–H in hydrated Portland cement paste is investigated in this study based on a large set of experimental data reported in literatures. C–S–H is taken as the major binder of alkali ions in normal Portland cement paste [3]. New models are proposed for the alkali binding in the C–S–H accounting for the dynamic equilibrium between the solid phase and the liquid. Formation of syngenite and the “U-phase” (a sodium-substituted AFm phase) can occur in the cement pastes with very high

* Corresponding author. Tel.: +86 27 87210782.

E-mail address: w.chen.whut@gmail.com (W. Chen).

alkali contents, or immersed in water with high alkali concentrations. This situation is hardly encountered in conventional cement pastes and is thus beyond the scope of this research.

The methods for predicting the alkali concentrations in the pore solution of hydrated Portland cement pastes proposed by Taylor [18] and further developed by Brouwers and Van Eijk [3] are updated with the new models proposed for the alkali binding in the C–S–H. They are used to investigate the effects of some relevant factors on the alkali concentrations as well.

2. Alkali binding in synthetic C–S–H

While it is difficult to measure the alkali-binding capacity of hydration products in Portland cement paste directly, experiments for this purpose with synthetic C–S–H gel were carried out. Stade [17] studied the incorporation of alkalis in the synthetic C–S–H and C–A–S–H gels. It was found that the amount of alkali hydroxide incorporated in C–S–H gels increased with decreasing calcium to silicon molar ratio (C/S). The alkali-binding capacity of the Al-containing C–S–H gel was smaller than the Al-free gel with equal C/S ratios. No obvious differences between the binding capacities for Na⁺ and K⁺ were observed in the experiments.

Hong and Glasser [7,8] studied the alkali binding in synthetic C–S–H and C–A–S–H gels as well. They used the concept of “distribution ratio” to describe the alkali-binding capacities of the synthetic gels, which is the ratio of concentrations of a solute distributed between two immiscible solvents, and is calculated as [7]:

$$Rd = \frac{\text{alkali in solid C-S-H}}{\text{alkali concentration in solution}} \text{ (mL/g)}. \quad (1)$$

The alkali-binding capacity of the alumina-free C–S–H was found to increase linearly with increasing alkali concentrations in the solution. This linear relation was concluded from the approximately constant distribution ratios of C–S–H with fixed C/S ratios. However, if alumina was incorporated into C–S–H, which takes place in hydrated Portland cement paste [14,20], the C–A–S–H gels had obviously enhanced alkali-binding capacity, which is in contrast to the conclusion of Stade [17]. This enhancement was more obvious for C–A–S–H gels with low C/S ratios. On the one hand, more alkali ions were bound in all C–S–H and C–A–S–H gels with increasing alkali concentrations in the solution. On the other hand, the distribution ratio decreased with increasing alkali concentrations in the pore solution, which indicates that a linear relationship between the binding capacity and the alkali concentrations is questionable. There was no significant difference between the alkali-binding capacity of C–S–H for Na⁺ and K⁺, similar to the conclusion of Stade [17].

A possible explanation for the different observations found in the experiments of Stade [17] and Hong and Glasser [7,8] is the way of preparing the C–S–H gel. Stade [17] made the C–S–H gel at 150 °C by the autoclave reaction of CaO and silica, and at 80 °C by precipitation from sodium silicate solutions with calcium chloride. Hong and Glasser [7] prepared the C–S–H gel by mixing Ca(OH)₂ and a very reactive, high surface area silica gel in double-distilled, CO₂-free water, sealed for 12 months at 20 ± 2 °C with regular agitation. The C–A–S–H gel was prepared by mixing the synthetic C–S–H gel with an initially amorphous alumina gel, followed by regular agitation for up to one year at 20 °C [8]. The difference in the way of preparation and the prevailing temperature may have a significant influence on the heterogeneity and structure of the C–S–H gel [5,21]. The influence of different preparation temperature was observed in the experiments of Stade [17] as well.

Furthermore, the alkali concentrations used by Hong and Glasser [7,8] for determining the alkali binding capacity was between 1 and 300 mmol/L for the C–S–H gel and between 15 and 300 mmol/L for the C–A–S–H gel. The alkali concentrations in the hydrated cement

pastes under investigation are frequently beyond this range because normally they are evaluated due to their high alkali oxide contents, which can potentially induce ASR in concrete. Therefore, high alkali concentrations are more relevant. The distribution ratio in real hydrated cement pastes may be significantly different from that of synthetic ones.

3. Alkali binding in hydrated Portland cement paste

Taylor [18] proposed a method for determining the alkali binding capacities of hydrated Portland cement paste more than one day old. An alkali partition theory was proposed, according to which part of the alkali ions are bound in the solid hydration products and the others exist in the pore solution.

The moles of alkali ions released by the hydration of the Portland cement which become available for the pore solution (n_i^r) were predicted as:

$$n_i^r = n_i^T \cdot \{f_i^{\text{sul}} + \sum_{j=1}^4 [f_{ij} \cdot (1 - f_i^{\text{sul}}) \cdot \alpha_j]\} \quad (2)$$

in which n_i^T is the total amount of alkali ion i (Na⁺ or K⁺) in the anhydrous cement; f_i^{sul} is the fraction of alkali as sulfate; f_{ij} is the fraction of alkali ion i (to the amount of alkali ions in clinker as non-sulfates) in clinker phase j ; and α_j is the hydration degree of phase j . Empirical methods for determining the parameters f_i^{sul} , f_{ij} and α_j were given by Taylor [18].

The alkali ions released by the cement hydration are divided into two parts: those in the solution and those bound in the hydration products. Hence:

$$n_i^r = n_i^b + n_i^s \quad (3)$$

in which n_i^b is the mole of alkali ions bound in products and n_i^s is the moles in the solution, which reads:

$$n_i^s = C_i \cdot V_w \quad (4)$$

in which C_i (mol/L) is the concentration of alkali ion i and V_w is the volume of pore solution (L).

Taylor [18] assumed that the moles of bound alkali ions are proportional to their concentrations and the mass of hydration products. Thus:

$$n_i^b = Ba_i \cdot C_i \cdot F \quad (5)$$

in which Ba_i is a binding factor (L) of alkali i and F is the quantity ratio of the hydration products to that after the complete hydration of the Portland cement. Substituting Eqs. (3) and (4) into Eq. (5) gives:

$$Ba_i = \frac{n_i^r - C_i \cdot V_w}{C_i \cdot F}. \quad (6)$$

Constant values of Ba_i for both Na⁺ and K⁺ were used by Taylor [18], implying that they are independent to the alkali concentrations. The amount of bound alkalis is linearly related to the mass of hydration products. The theoretical basis of the assumption about this linear dependency is not clear, as stated by Taylor [18]. The values of Ba_i were calculated from the experimental results reported in various literatures.

Brouwers and Van Eijk [3] investigated the alkali binding capacities of hydrated Portland cement pastes following the same method proposed by Taylor [18]. However, they used a three-dimensional computer model CEMHYD3D, which was developed at NIST [2] to predict the hydration degree of cement, the amount of alkali ions released by the cement hydration, the amount of C–S–H

and volume of pore solution. Furthermore, they proposed that only the hydration product C–S–H is able to bind alkalis, instead of the relative fraction of C–S–H and AFm phases formed in the paste. They also used the concept of distribution ratio to compute the amounts of alkalis bound in C–S–H as:

$$n_i^b = Rd_i \cdot C_i \cdot m_{C-S-H} \quad (7)$$

in which m_{C-S-H} is the mass of C–S–H in the hydrated paste and Rd_i is the distribution ratio of alkali i (Na^+ or K^+). The values of the distribution ratio were computed as:

$$Rd_i = \frac{n_i^r - C_i \cdot V_w}{C_i \cdot m_{C-S-H}} \quad (8)$$

Similar to the theory of Taylor [18], Brouwers and Van Eijk [3] concluded constant values of Rd_i , implying that the alkali-binding capacity of C–S–H is linearly proportional to the alkali concentrations in the solution, which is still to be verified.

4. Determining the alkali binding capacities from experimental results

Much research work has been done to investigate the evolution of alkali concentrations in the pore solution of hydrated Portland cement pastes. In this study, the experimental data reported in a large number of research work [1,4,9,10,12,15,16] were collected and used to determine the alkali binding capacity of the hydration product C–S–H. Different cements and water to cement ratios were used in these experiments. Hence, it is expected that the results derived from these data give a general figure about the alkali binding capacities of hydrated Portland cement paste.

The oxide compositions of the Portland cements used in the experiments [1,4,9,10,12,15,16] are listed in Table 1 together with the recipes of the pastes, the fineness of the cements and the curing temperatures. All the pastes were cured in a sealed environment. Pore solutions were collected at the planned ages using the liquid expression method and the alkali concentrations were analyzed.

The hydration of these cement pastes are firstly simulated by using the computer model CEMHYD3D. It is a pixel-based digital model

Table 1
Properties of Portland cements, w/c ratio of the paste and curing temperature.

Num.	Bogue composition (m/m%)				Alkalis (m/m%)		Blaine fineness (m ² /kg)	w/c	Temperature (°C)
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Na ₂ O	K ₂ O			
1 ^a	56.8	19.7	6.9	11.3	0.43	1.23	380 ^b	0.42	23
2 ^a	70	8.8	7.4	11.3	0.2	0.47	380 ^b	0.42	23
3 ^c	54.5	21.3	10.9	9.2	0.21	0.82	321	0.4	22
4 ^c	54.5	21.3	10.9	9.2	0.21	0.82	321	0.45	22
5 ^c	54.5	21.3	10.9	9.2	0.21	0.82	321	0.56	22
6 ^d	55	15	7.9	8.1	0.08	1.12	300	0.5	20
7 ^e	58	16	7	12	0.16	0.51	312	0.35	22
8 ^f	63.8	12.4	11	8.8	0.14	0.95	370	0.5	20
9 ^f	69.8	6.8	9.6	9.7	0.19	1.22	369	0.5	20
10 ^f	65.8	15.2	8.7	10.2	0.64	0.78	380 ^b	0.5	20
11 ^g	64.3	17.3	8.5	9.9	0.32	0.6	310	0.4	23
12 ^{h,i}	55.1	25	9.7	10.2	0.25	1.27	380 ^b	0.5	20
13 ^{h,j}	55.1	25	9.7	10.2	0.25	1.27	380 ^b	0.5	20

^a Taken from Bérubé et al. [1].

^b Assumed value.

^c Taken from Larbi et al. [9].

^d Taken from Lothenbach and Winnefeld [12].

^e Taken from Rothstein et al. [15].

^f Taken from Schäfer [16].

^g Taken from Diamond [4].

^h Taken from Longuet [10].

ⁱ 4.5 m/m% gypsum added.

^j 8.6 m/m% gypsum added.

which uses the random walking and phase transition algorithm to simulate the dissolution, transition and precipitation processes during cement hydration. The model takes into account the effects of cement composition, temperature, fineness of cement and the sealing conditions of the paste on the hydration. For more details of this computer model, the readers are referred to the work of Bentz [2]. The fineness of cements which was not reported is assumed to be 380 m²/kg, corresponding approximately to CEM I 32.5R produced in the Netherlands. The hydration degree of clinker phases (α_j), the mass of C–S–H (m_{C-S-H}) and the volume of pore solution (V_w) are taken from the model predictions.

Because it was consistently assumed that the number of moles of bound alkalis in the hydration products is proportional to the alkali concentrations in the solution, this line is firstly followed. A similar concept as the “binding factor” is used for facilitating the discussion, called “Molar concentration” (Ma) of alkalis in C–S–H, physically representing the number of moles of alkali per unit mass of the binder. If the binding capacity of the C–S–H gel is irrelevant to the concentration of the alkali, the relationship between Ma and the concentration should be linear.

The values of Ma are calculated according to its definition as:

$$Ma = \frac{n_i^b}{m_{C-S-H}} \text{ (mmol / g)}. \quad (9)$$

One can see by comparing Eqs. (7) and (9) that actually:

$$Ma = Rd \cdot C_i. \quad (10)$$

Substituting Eqs. (3) and (4) into Eq. (9) gives:

$$Ma_i = \frac{n_i^r - C_i \cdot V_w}{m_{C-S-H}}. \quad (11)$$

If the alkali concentration C_i is known (for example, measured in the experiments), Ma is computed with Eq. (11).

The calculated values of Ma for Na^+ and K^+ from the experimental data reported in the literatures [1,4,9,10,12,15,16] are plotted as a function of the alkali concentrations in Fig. 1.

It can be seen in Fig. 1(a) that there is a linear relationship between the Ma of Na^+ in C–S–H and its concentration, implying a constant binding capacity of C–S–H for Na^+ . This linear binding model is in agreement with the hypothesis by Taylor [18] and Brouwers and Van Eijk [3]. A linear regression analysis of the data presented in Fig. 1(a) gives:

$$Ma_N = 0.45C_i \text{ (mmol / g)}. \quad (12)$$

Hence, based on Eq. (10),

$$Rd_N = 0.45 \text{ (mL / g)}. \quad (13)$$

The value of Rd_N is close to that used by Brouwers and Van Eijk [3] (0.39 mL/g), which was computed from the work of Hong and Glasser [7].

However, a linear relationship between the Ma and the concentration cannot be discerned for K^+ (Fig. 1(b)). The constant binding capacity of C–S–H to the K^+ is not verified. Most likely, a non-linear model for the binding of K^+ in C–S–H should be employed.

The distribution ratio of K^+ (Rd_k) is computed with Eq. (10) and plotted in Fig. 2. It can be seen that the distribution ratio of K^+ (Fig. 2) decreases with increasing K^+ concentrations, indicating a non-linear binding of C–S–H for K^+ . The non-linear relation in Fig. 2 is fitted with the following expression:

$$Rd_k = 0.20C_i^{-0.76} \text{ (mL / g)}. \quad (14)$$

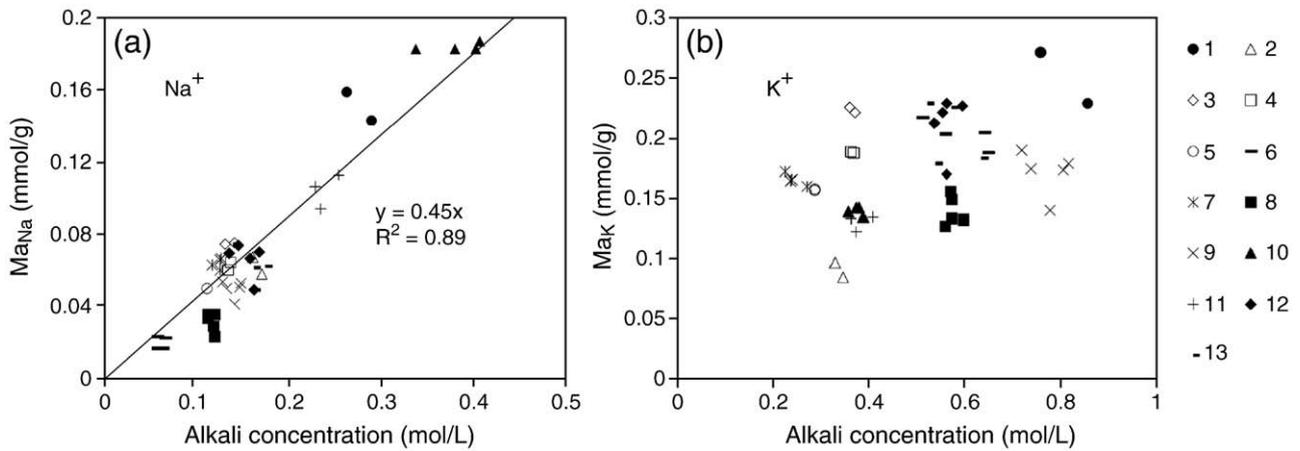


Fig. 1. Values of Ma versus alkali concentration in solution. Numbers in the legend correspond to the numbering of cement in Table 1.

And substituting Eq. (14) into Eq. (10) gives:

$$Ma_k = 0.20C_i^{0.24} \text{ (mmol/g)} \quad (15)$$

The expression above complies with the well-known Freundlich isotherm, which is widely used to describe the adsorption of solutes in solution by solid phases. It has the general form of:

$$C_s = K_f \cdot C^n \quad (16)$$

where C_s is the concentration in the solid phase; C is the concentration in the fluid phase; K_f is the Freundlich adsorption constant and n is the Freundlich exponent. If $n = 1$, the Freundlich isotherm reduces to the linear isotherm. The Freundlich isotherm often represents an initial surface adsorption of alien ions followed by a condensation effect resulting from extremely strong solute–solute interaction.

Experimental data about the binding capacity of hydrated Portland cement paste in regard to different alkali concentrations in the pore solution is difficult to find. The reported data by Schäfer [16] and Longuet [10] are measured with different recipes. However, experimental data on the binding of chloride ion in the hydrated Portland cement paste have recently become available. Chidiac et al. [13]

measured the amount of bound Cl^- in the hydrated Portland cement paste that was equilibrated with solutions containing different amounts of chloride ions. Paste samples were made and equilibrated with the solution at 23 °C. Five different concentrations of chloride were used, ranging between 0 and 3.0 mol/L. The distribution ratio (Rd_{Cl}) is calculated from the data reported by Chidiac et al. [13] and is plotted in Fig. 3. The calculated values of Rd are also fitted with Eq. (16), yielding:

$$Rd_k = 0.25C_{Cl}^{-0.62} \text{ (mL/g)} \quad (17)$$

in which C_{Cl} is in mol/L. It can be seen that the binding characteristic of hydrated Portland cement paste on chloride ions are very similar to that on the potassium. Both the trend and the fitted values are in good quantitative agreement, though they concern the binding of the anion (Cl^-) instead of the cations (Na^+ and K^+). Hence, one might conclude from the comparison that the Freundlich isotherm is appropriate for the binding of other ions as well.

5. An updated method for predicting the alkali concentrations

The alkali-binding capacity of the hydration products is an essential factor in the methods proposed by Taylor [18] and developed by Brouwers and Van Eijk [3]. In both methods, the alkali-binding factors are set to be constant based on the experimental results by using the synthetic C–S–H [3], or constant values largely based on

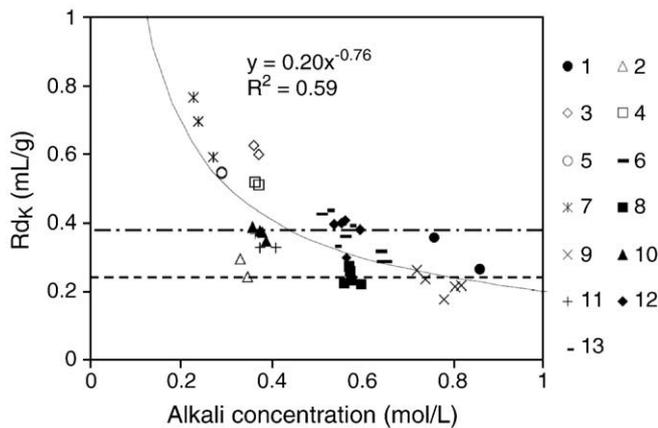


Fig. 2. Relationship between the calculated values of Rd and the concentration of K^+ . Numbers in the legend correspond to the numbering of cement in Table 1. “- - - -”: values used by Brouwers and Van Eijk [3]; “-”: values calculated from the work of Taylor [18], “- -”: values suggested in the present work.

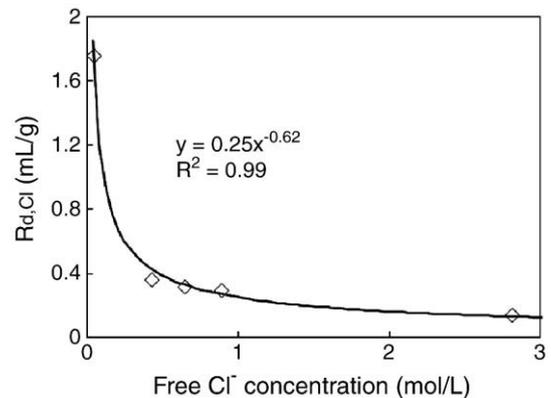


Fig. 3. Distribution ratio of chloride ions in hydrated Portland cement paste at 23 °C, calculated from the work of Chidiac et al. [13].

assumptions [18]. However, the constant alkali-binding capacity of C–S–H is not supported by the experimental results of Hong and Glasser [7] and Stade [17]. New methods for determining the binding factors of C–S–H to Na^+ and K^+ in hydrated Portland cement pastes proposed in this study should be followed.

The method used by Taylor [18] and Brouwers and Van Eijk [3] are updated with the newly proposed models in this study. The concentration of Na^+ in the pore solution is computed as:

$$C_{\text{Na}} = \frac{n_{\text{Na}}^r}{V_w + 0.45m_{\text{C-S-H}}} \quad (18)$$

and the concentration of K^+ is computed by solving the equation:

$$C_{\text{K}} \cdot V_w + 0.20(C_{\text{K}})^{0.24} \cdot m_{\text{C-S-H}} = n_{\text{K}}^r \quad (19)$$

Taylor [18] determined the value of the binding factor from measurements in nine laboratories and validated it with four batches of samples in these laboratories. A similar idea is used here by validating the new method with 6 of the 13 recipes in Table 1. These 6 recipes include cements from different literatures and with varying alkali contents. Eqs. (18) and (19) are used for predicting the alkali concentrations in the pore solution. The hydration of these six cement pastes is simulated with the CEMHYD3D and the simulation results are used as inputs for predicting the alkali concentrations in the pore solution.

The predicted alkali concentrations are included in Fig. 4 (solid lines) together with the experimental measurements (symbols). It can be seen that the concentrations are predicted fairly well for both the Na^+ and K^+ ions while to a better extent for Na^+ if we look at the results closely. The difference between the predicted K^+ concentrations and the measured ones at early ages are mostly due to the uncertainties in determining the fraction of alkalis as readily-soluble sulfates (f_i^{sol} in Eq. (2)) in the clinker. According to Pollitt and Brown (1969) (referenced by Taylor [19]), the fraction of Na_2O as sulfates in clinker are mostly in the range of 0.2 to 0.4, but that of K_2O can be in the range of 0.2 to 1. Employing the set of empirical equations proposed by Taylor [18] for determining f_i^{sol} could result in remarkable uncertainty for computing the total amount of alkalis released by the cement hydration at early ages. However, at ages later than 28 days, most of the clinker has hydrated releasing most of the alkalis. Hence, the effects of using the empirical equations are minimized for late ages. It should be noted that the development of the K^+ concentration in the pore solution of Cement 7 is abnormal compared to the other five cements. The K^+ concentration declined remarkably after 7 days, which is probably due to the low K_2O content in the clinker compared to the others.

The predicted concentrations of Na^+ and K^+ with the binding models of Brouwers and Van Eijk [3] are included in Fig. 4 as well (dashed lines). It can be seen that in general the predictions obtained with the updated method agree better to the measurements than those obtained with the method of Brouwers and Van Eijk [3]. The advantage of the updated methods is more obvious for the K^+ ion than for the Na^+ . Two factors contribute: (1) the constant distribution ratio of the Na^+ ion concluded in this study (0.45 mL/g) is close to the value used by Brouwers and Van Eijk [3] (0.39 mL/g). (2) the distribution ratios of K^+ spread in a wide range (from about 0.2 mL/g to 0.7 mL/g), which diverse remarkably from the constant value (0.38 mL/g) used by Brouwers and Van Eijk [3].

It is concluded that the update of the predictive model for the alkali concentrations in the pore solution of hydrated Portland cement paste improves the reliability of the original method by Taylor [18] and successive method by Brouwers and Van Eijk [3]. The linear method by Taylor [18] and Brouwers and Van Eijk [3] is valid for

predicting the Na^+ concentration and the non-linear method given in Eq. (19) should be followed for modeling the K^+ concentration.

6. Application of the updated method

Effects of different factors, such as the w/c ratio of the paste, the mineral composition of cement and the type of alkali oxides, on the alkali concentration in the pore solution are often topics of various researches and are investigated with the updated method in this study. Cement Z1 from the work of Schäfer [16] (Cement 8 in Table 1) is used as example in the following discussion, and the complete hydration of cement is assumed to occur, corresponding roughly to the hydration age of one year.

6.1. w/c ratio of the cement paste

Low w/c ratios are more and more commonly used in concrete to achieve high-strength and low porosity. While the advantage of low w/c ratios has been widely investigated, its influence on the alkali concentrations has not yet been completely clarified.

All parameters (for example, clinker composition and temperature) except the w/c ratio of the paste are kept the same, so that the investigation is focused on the effect of w/c ratio. The predicted alkali concentrations are plotted in Fig. 5(a).

It can be seen that while the w/c ratio has only a very mild effect on the Na^+ concentration, the effect on the K^+ concentration is obvious. The concentration of K^+ increases dramatically with decreasing w/c ratios. The increase is expected because the reduced w/c ratios decrease the volume of water available for the alkali ions.

The different trends for Na^+ and K^+ are caused by the different binding capacities of C–S–H. On the one hand, it can be seen in Fig. 1 that the binding capacity increases approximately linearly with increasing concentrations of Na^+ . Hence, a large part of the additional Na^+ induced by the increased amount of cement is bound in C–S–H. On the other hand, the binding capacity of C–S–H to K^+ changes only very slightly with K^+ concentrations. The flat changes of Na^+ concentration are also partly due to its low level in the pore solution.

6.2. Mineral composition of clinker

The influence of mineral composition on the alkali concentrations is investigated with the updated methods in this study. The w/c ratio is 0.5. The C_3S content in the clinker ranges from 30 m/m% to 70 m/m%, while the C_2S content ranges from 46 m/m% to 6 m/m%, accordingly. They total to 76 m/m% of the clinker. The C_3A and C_4AF contents in the clinker are not changed. It can be seen that the concentrations of both Na^+ and K^+ increase with increasing C_3S content in the clinker due to the reduced amount of C–S–H formed in the paste (Fig. 5(b)). The hydration of C_3S per unit mass can produce less C–S–H and more CH than that of C_2S . Hence, less alkali ions are bound in C–S–H and more is available for the pore solution.

However, the influence of shifting from C_3S to C_2S on the alkali concentrations is very limited because the hydration of C_3S consumes less water than that of C_2S [22], leaving more water available for the pore solution, which in turn dilutes the alkali ions in the solution.

6.3. Alkali type

In various specifications/standards, the total alkali content in the cement is regulated as Na_2O -equivalent. However, the alkali types are not distinguished. Different types of alkalis are sometimes added to cement to achieve high levels of alkalis to evaluate the potential risk of ASR. Both Na^+ and K^+ are used, mostly in the form of NaOH and KOH . Little attention is paid to the different types of alkalis, though the resultant alkalinity of the pore solution may be quite different.

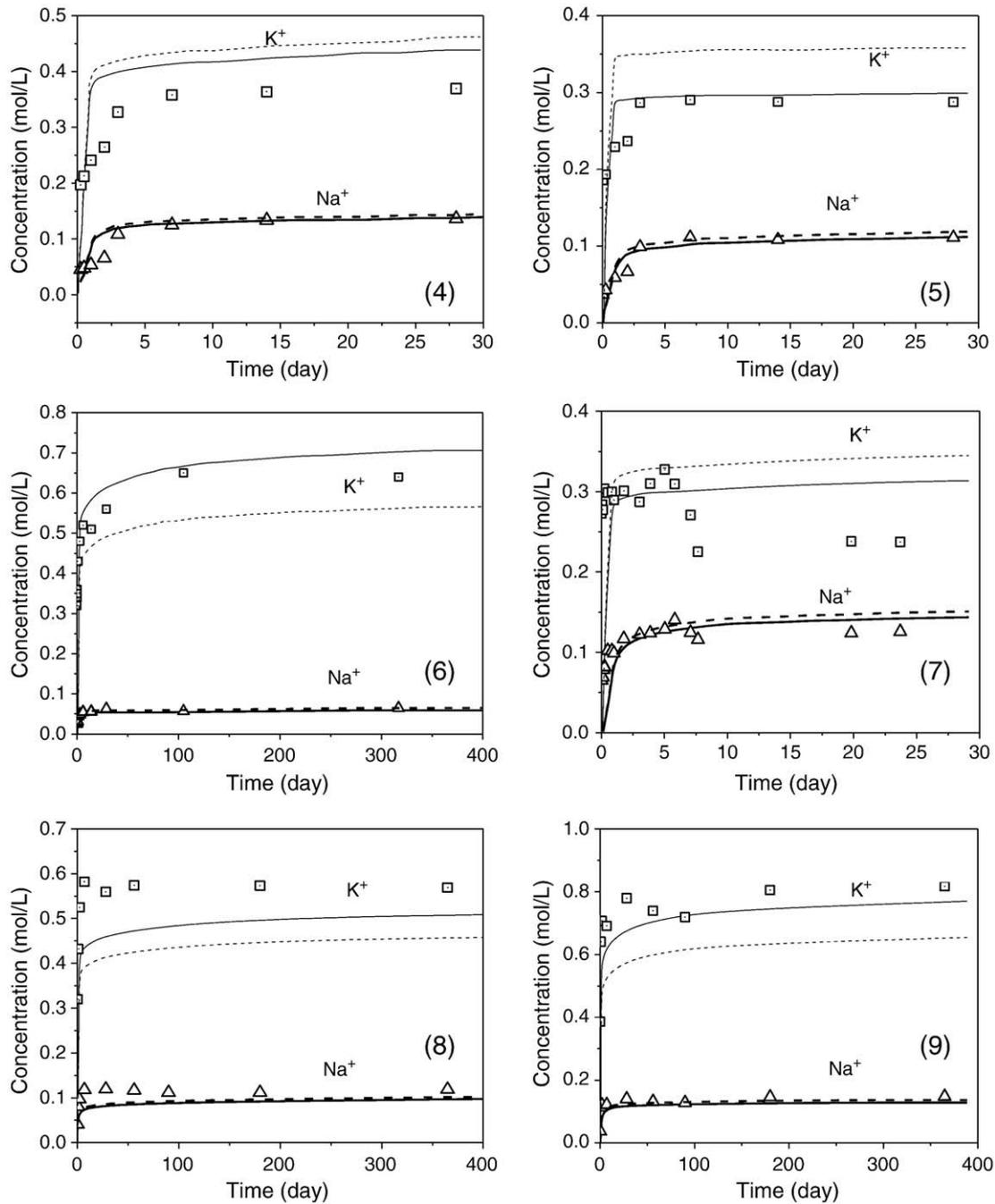


Fig. 4. Predicted and measured concentration of alkali ion in the pore solution with Cements 4–9 from Table 1.

The influence of alkali types on the alkali concentration and the alkalinity is discussed. The alkali level of Cement 8 is intentionally raised from 0.77 m/m% to 1.2 m/m% as $\text{Na}_2\text{O}_{\text{eq}}$, i.e. $x_{\text{Na}_2\text{O}} + 0.658x_{\text{K}_2\text{O}} = 1.2\%$, in which $x_{\text{Na}_2\text{O}}$ and $x_{\text{K}_2\text{O}}$ are the mass percentages of Na_2O and K_2O in the cement, respectively. $x_{\text{Na}_2\text{O}}$ takes a value starting from 0.14% to 0.8% and the value of $x_{\text{K}_2\text{O}}$ is calculated accordingly. The w/c ratio of the paste is 0.5.

The predicted alkali concentrations are plotted in Fig. 5(c) with changing Na_2O contents in the clinker in which the total alkali content as $\text{Na}_2\text{O}_{\text{eq}}$ remains the same. It can be seen that the concentration of Na^+ increases steadily and the concentration of K^+ decreases sharply if K_2O is partially replaced by Na_2O . Moreover, the total alkali concentration ($C_{\text{Na}} + C_{\text{K}}$) decreases. The drop of the total alkali concentration is explained by the different binding capabilities of C–S–H to K^+ and Na^+ . As revealed in the previous sections, the

binding of Na^+ in C–S–H is linearly related to the concentration of Na^+ . Hence, it is perceivable from Eq. (18) that the value of C_{Na} increases linearly with n_{Na}^f . However, another line is followed for K^+ . With decreasing n_{K}^f and C_{K} , the binding capacity of C–S–H is actually enhanced (Fig. 2). Thus, more K^+ is bound in the C–S–H and less is available for the pore solution.

The different behaviors of C–S–H concerning the binding of Na^+ and K^+ are also observed in the experiments of Bérubé et al. [1]. They raised the alkali levels in the cement pastes (1.25 m/m% as $\text{Na}_2\text{O}_{\text{eq}}$ to the mass of cement) by adding NaOH or KOH solution into the mixing water separately. The total alkali concentration ($C_{\text{Na}} + C_{\text{K}}$) in the pore solution collected from the pastes was significantly different. For pastes cured at 38 °C up to 91 days, the total alkali concentration if KOH solution is added is 51.7%, 11.8% and 9.5% higher than that of the paste if NaOH solution is added at the age of 7, 28 and 91 days,

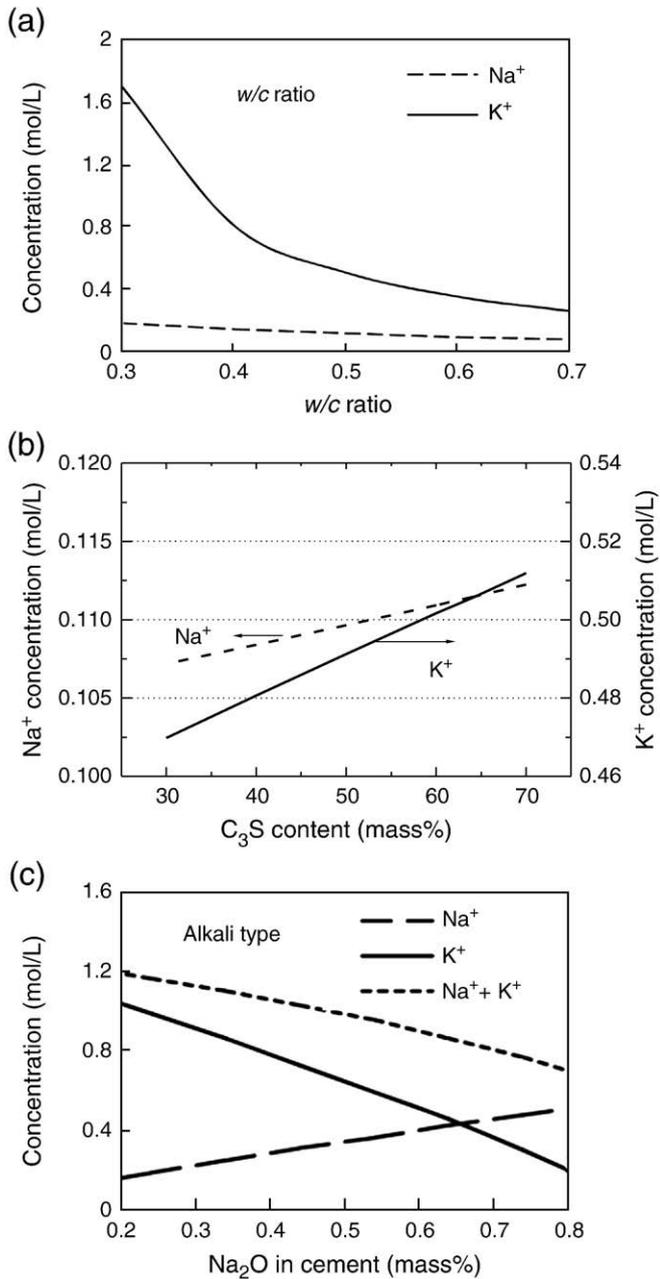


Fig. 5. Effect of different factors on the alkali concentrations in pore solution of hydrated Portland cement paste. (a) w/c ratio; (b) C₃S content in clinker; (c) alkali type. Predicted with Cement 8 in Table 1.

respectively. The raised alkali concentrations in the pore solution indicate that the hydration product C–S–H can bind less K⁺ than Na⁺ at high concentrations, and thus more alkalis remain in the solution.

The effect of alkali types in cement on the alkalinity of the pore solution must be kept in mind when additional alkali oxides are added into the paste to raise the alkali levels. K⁺ is preferred since the resulting alkali concentration is higher than Na⁺, eliminating the risk of underestimating the alkali levels.

7. Conclusions

It is generally recognized that part of the alkalis released by the cement hydration is bound in the solid hydration products and is thus not available for the pore solution. The alkali binding capacities of the hydration products are essential for understanding the interactions between the solids and the ions dissolved in the pore

solution. The alkali binding capacity of the C–S–H gel is investigated in this study following the classical alkali partition theory proposed by Taylor [18] and further developed by Brouwers and Van Eijk [3] using a large set of experimental data reported in different literatures. It was revealed that a linear binding isotherm should be employed for the binding of Na⁺ in C–S–H and a new value of the binding capacity was proposed. However, for the binding of K⁺ in C–S–H, the Freundlich isotherm should be followed and a new model for determining the binding capacity of K⁺ was established. The method for predicting the alkali concentrations in the pore solution of hydrated Portland cement pastes were updated with the new findings of this research. It was used to investigate the effects of various factors on the alkali concentrations to illustrate the possible applications of the updated method.

Acknowledgements

The authors wish to thank the following institutions for their financial support of the present research: Dr. ir. Cornelis Lely Foundation, Delta Marine Consultants, Betoncentrale Twenthe, Rokramix, Dutch Ministry of Infrastructure, SenterNovem Soil+, Jaartsveld Groen en Milieu, the National Natural Science Foundation of China (Project 50802067) and the National Basic Research Program (973) of China (Project 2009CB623200).

References

- [1] M.A. Bérubé, C. Tremblay, B. Fournier, M.D. Thomas, D.B. Stokes, Influence of lithium-based products proposed for counteracting ASR on the chemistry of pore solution and cement hydrates, *Cem. Concr. Res.* 34 (9) (2004) 1645–1660.
- [2] D.P. Bentz, Guide to using CEMHYD3D: a three-dimensional cement hydration and microstructure development modelling package, Report NISTIR 5977, NIST, Gaithersburg, MD, U.S., 1997.
- [3] H.J.H. Brouwers, R.J. Van Eijk, Alkali concentrations of pore solution in hydrated OPC, *Cem. Concr. Res.* 33 (2003) 191–196.
- [4] S. Diamond, Effect of two Danish fly ashes on alkali contents of pore solutions of cement-flyash pastes, *Cem. Concr. Res.* 11 (1981) 383–394.
- [5] K. Fujii, W. Kondo, Heterogeneous equilibria of calcium silicate hydrate in water at 30 °C, *J. Chem. Soc. Dalton Trans.* 2 (1984) 645–651.
- [6] F.P. Glasser, The pore fluid in Portland cement: its composition and role, *Proc. 11th ICCO, Durban, South Africa, 2003*, pp. 341–352.
- [7] S.Y. Hong, F.P. Glasser, Alkali binding in cement pastes: part I, the C–S–H phase, *Cem. Concr. Res.* 29 (1999) 1893–1903.
- [8] S.Y. Hong, F.P. Glasser, Alkali sorption by C–S–H and C–A–S–H gels: part II, role of alumina, *Cem. Concr. Res.* 32 (2002) 1101–1111.
- [9] J.A. Larbi, A.L.A. Fraay, J.M. Bijen, The chemistry of the pore fluid of silica fume-blended cement systems, *Cem. Concr. Res.* 20 (1990) 506–516.
- [10] P. Longuet, La protection des armatures dans le béton armé élaboré avec des ciments de laitier, *Silic. Ind.* 7/8 (1976) 321–328.
- [11] P. Longuet, L. Burglen, A. Zelwer, The liquid phase of hydrated cement, *Rev. Mater. Constr.* 676 (1973) 35–41.
- [12] B. Lothenbach, F. Winnefeld, Thermodynamic modelling of the hydration of Portland cement, *Cem. Concr. Res.* 36 (2) (2006) 209–226.
- [13] S.E. Chidiac, D.K. Panesar, H. Zibara, Chloride binding and its effects on the pore structure of concrete containing GGBFS, *Cem. Concr. Res.* (submitted for publication).
- [14] I.G. Richardson, G.W. Groves, Microstructure and microanalysis of hardened cement pastes involving ground granulated blast-furnace slag, *J. Mater. Sci.* 27 (1992) 6204–6212.
- [15] D. Rothstein, J.J. Thomas, B.J. Christensen, H.M. Jennings, Solubility behavior of Ca-, S-, Al-, and Si-bearing solid phases in Portland cement pore solutions as a function of hydration time, *Cem. Concr. Res.* 32 (2002) 1663–1671.
- [16] E. Schäfer, Einfluss der Reaktionen verschiedener Zementbestandteile auf den Alkalihaushalt der Porenlösung des Zementsteins, Ph.D. thesis, Clausthal University of Technology, Clausthal-Zellerfeld, Germany, 2004.
- [17] H. Stade, On the reaction of C–S–H (di, poly) with alkali hydroxides, *Cem. Concr. Res.* 19 (5) (1989) 802–810.
- [18] H.F.W. Taylor, A method for predicting alkali ion concentrations in cement pore solutions, *Adv. Cem. Res.* 1 (1) (1987) 5–16.
- [19] H.F.W. Taylor, *Cement Chemistry*, Thomas Telford Ltd., London, 1997.
- [20] S. Wang, K.L. Scrivener, ²⁹Si and ²⁷Al NMR study of alkali-activated slag, *Cem. Concr. Res.* 33 (2003) 769–774.
- [21] J.F. Young, Investigations of calcium silicate hydrate structure using silicon-29 nuclear magnetic resonance spectroscopy, *J. Am. Ceram. Soc.* 71 (1988) 118–120.
- [22] H.J.H. Brouwers, The work of Powers and Brownard revisited: Part I. Cement and Concrete Research 34 (2004) 1697–1716.