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Cement & Concrete Composites 30 (2008) 353–359

Cement & Concrete Composites

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The use of thermodynamic analysis in assessing alkali contribution by alkaline minerals in concrete

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Received 16 November 2005; received in revised form 2 February 2007; accepted 14 March 2007
Available online 24 March 2007

Abstract

Using a thermodynamic method, the decomposition reactions of alkaline minerals in alkaline solution were studied, and the theoretical alkali contribution by alkaline minerals was analyzed also. It was indicated that the theoretical maximum alkali released from alkaline minerals in order was dawsonite > leucite > nepheline > dehydration analcime > paragonite > muscovite > jadeite > Na-feldspar > K-feldspar in alkaline solution with pH > 13. With the increasing of pH in alkaline solution, the maximum amounts of alkali released from alkaline minerals increase excluded nepheline. Furthermore, the maximum alkali contribution by alkaline minerals to concrete was calculated based on an aggregate content of 1850 kg/m^3. It was found that the maximum alkali contribution by alkaline minerals was affected mainly by the pore solution/aggregate ratio, then the pH level of pore solution. These results also suggest that using low water-to-cement ratio and preventing water from permeating into concrete could effectively restrain alkali released from aggregate.

Keywords: Thermodynamics; Alkali-aggregate reaction; Alkaline mineral; Aggregate; Alkali

1. Introduction

With the presence of potentially reactive aggregates, sufficient alkali in concrete pore solution and high humidity environment are essential conditions to initiate and sustain alkali-aggregate reaction (AAR) in concrete. In general, alkalies in concrete pore solution are mostly supplied by the cement, but chemical admixtures, mineral admixtures, aggregates, mixing water, and a moist external environment may also contribute alkalies to the pore solution. Using low-alkali cement with less than 0.6% Na_2O_e or limiting concrete alkali content is normal preventive measure against AAR in the presence of potentially reactive aggregates.

Based on numerous field and laboratory investigations, it is now a matter of fact that some aggregates may supply significant amounts of alkalies to the concrete pore solution and to cause a disruptive expansion [1–15]. It was often used to explain why many concrete structures which had been built with low-alkali cements (<0.6% Na_2O_e) and/or with cements supplying less than 3 kg/m^3 Na_2O_e, and/or with large amount of fly ashes, now show signs of being affected by AAR. Since the process of alkali contribution by aggregate has not been clearly understood, there is still no standard method to accurately predict the alkali contribution by aggregates.

A number of experimental procedures have been used in the past to estimate the alkali contribution by aggregates to the concrete pore solution [1–4,8,11]. According to these researchers, some alkali-bearing minerals or phases in aggregates may supply significant amounts of alkalies to the concrete pore solution with time, such as volcanic glasses, feldspars, micas, clay minerals, nepheline, dawsonite and zeolites. However, the number and type of

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doi:10.1016/j.cemconcomp.2007.03.003

aggregates tested were limited, and the test conditions, such as the aggregate fineness, the solution used for extraction, the aggregate/solution ratio, the temperature, and the test duration, varied greatly from one study to another. All these conditions could influence the rates of alkali leaching as well as the absolute amounts of alkalies released, the results obtained by these methods are not uniform. There is still no an approved method to estimate the amounts of alkalies that can be supplied to the concrete pore solution by the aggregates.

Feldspar mineral is an important rock component and widely exists in igneous rock; many thermodynamic researches on its decomposition under acid or neutral environment had been done in mineralogy, petrology, and geochemistry [16,17]. In this paper, the decomposition of different types of alkaline minerals in high pH solutions was studied using a thermodynamic method. The theoretically maximum amounts of alkalies released from alkaline minerals and some possible influences on alkali releasing from these alkaline minerals to concrete pore solution were analyzed.

2. Basic thermodynamic parameters and calculation method

Thermodynamic data adopted in this paper were taken from reference (see [18,19]) and shown in Table 1.

The thermodynamic method used in the study is shown as follows.

For reaction type, $aA + bB = mM + nN$, the molar reaction Gibbs function was changed into:

$$\begin{aligned}\Delta G^0_{298} &= \sum(\Delta G^0_{298})_{\text{product}} - \sum(\Delta G^0_{298})_{\text{reactor}} \\ &= m\Delta G^0_{298,m} + n\Delta G^0_{298,n} - a\Delta G^0_{298,a} - b\Delta G^0_{298,b}\end{aligned} \tag{1}$$

reaction equilibrium constant

$$K^0 = \exp(-\Delta G^0_{298,1}/RT) = \frac{\alpha_M^m \cdot \alpha_N^n}{\alpha_A^a \cdot \alpha_B^b}. \tag{2}$$

Table 1
Related thermodynamic data

Structural formula	ΔG^0_{298} (kJ mol^{-1})	Structural formula	ΔG^0_{298} (kJ mol^{-1})
OH^-	−234.007	K-feldspar, $KAlSi_3O_8$	−4037.681
H^+	6.262	Nepheline, $NaAlSiO_4$	−2046.01
H_2O (l)	−307.856	Na-feldspar, $NaAlSi_3O_8$	−3999.731
K^+	−277.116	Dehydration analcime, $NaAlSi_2O_6$	−3038.666
Na^+	−252.437	Leucite, $KAlSi_2O_6$	−2990.744
Al^{3+}	−418.320	Dawsonite, $NaAlCO_3(OH)_2$	−1766.108
$AlOH^{2+}$	−710.464	Jadeite, $NaAlSi_2O_6$	−3072.556
$Al(OH)_2^+$	−993.985	Muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$	−5600.964
$Al(OH)_3$	−1274.461	Paragonite, $NaAl_2(AlSi_3O_{10})(OH)_2$	−5562.007
$Al(OH)_4^-$	−1537.784	HCO_3^-	−586.848
$H_2SiO_4^{2-}$	−1410.599	CO_3^{2-}	−527.834
$H_3SiO_4^-$	−1471.558	$H_4SiO_{4,aq}$	−1521.442

In which α_i represents the activity degree of i ion when the reaction reaches equilibrium.

For the decomposition of alkaline mineral under high alkaline conditions, taking account of the relationship between the ion concentration and the activity degree α_i under 298 K, the following calculations was carried out:

$$I = \frac{1}{2}\sum C_i Z_i^2 \tag{3}$$

$$-\frac{\log \gamma_i}{Z_i^2} = \frac{0.511I}{1+1.5I} - 0.2I \tag{4}$$

In the equation above, 'C_i', 'Z_i' represent the volume mole concentration of i ion and its charge respectively, 'I' represents the ionic intensity, 'γ_i' is the activity degree coefficient of i ion. This formation is only suitable for the approximate calculation at temperature of 298 K [20].

3. Thermodynamic analysis on influence of pH on ion release from alkaline minerals

Under alkali condition, the decomposition types of various alkaline minerals depend on the specific condition. Using thermodynamic method, the decomposition reactions of alkaline minerals at 298.15 K will be discussed next.

3.1. Relationship between the distribution of aluminum ions and pH

Aluminum ions existing in solution mainly in the form of Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$ and so on, these formations transformed reciprocally as:

$$Al^{3+} + H_2O \Longleftrightarrow AlOH^{2+} + H^+ \tag{5}$$

In Eq. (5), $\Delta G^0_{298} = 21.974$ kJ/mol and $K^0 = 1.413 \times 10^{-04}$.

$$AlOH^{2+} + H_2O \Longleftrightarrow Al(OH)_2^+ + H^+ \tag{6}$$

In Eq. (6), $\Delta G^0_{298} = 30.597$ kJ/mol and $K^0 = 4.359 \times 10^{-06}$.

$$Al(OH)_2^+ + H_2O \Longleftrightarrow Al(OH)_3H^+ \tag{7}$$

In Eq. (7), $\Delta G^0_{298} = 33.642$ kJ/mol and $K^0 = 1.276 \times 10^{-04}$.

$$Al(OH)_3 + H_2O \Longleftrightarrow Al(OH)_4^- + H^+ \tag{8}$$

In Eq. (8), $\Delta G^0_{298} = 50.795$ kJ/mol and $K^0 = 1.261 \times 10^{-09}$.

The concentrations of ions with various forms in the solution lies in their total concentrations and their distribution factor λ_i, the relationship could be described as $C_i = \lambda_i C_{\text{total}}$. Under certain temperature and pressure, λ_i is a function of the pH values. The relationship between λ_i and the pH could be calculated based on the above equations. The result is shown in Fig. 1a.

According to Fig. 1a, it is obvious that $Al(OH)_4^-$ is the main form of aluminum ions in alkaline solution with pH > 12, and the distribution factor increase with the pH increases. In contrast, the distribution factor of $Al(OH)_3$ decreases, very little Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ exist in solution when the pH is higher than 12.

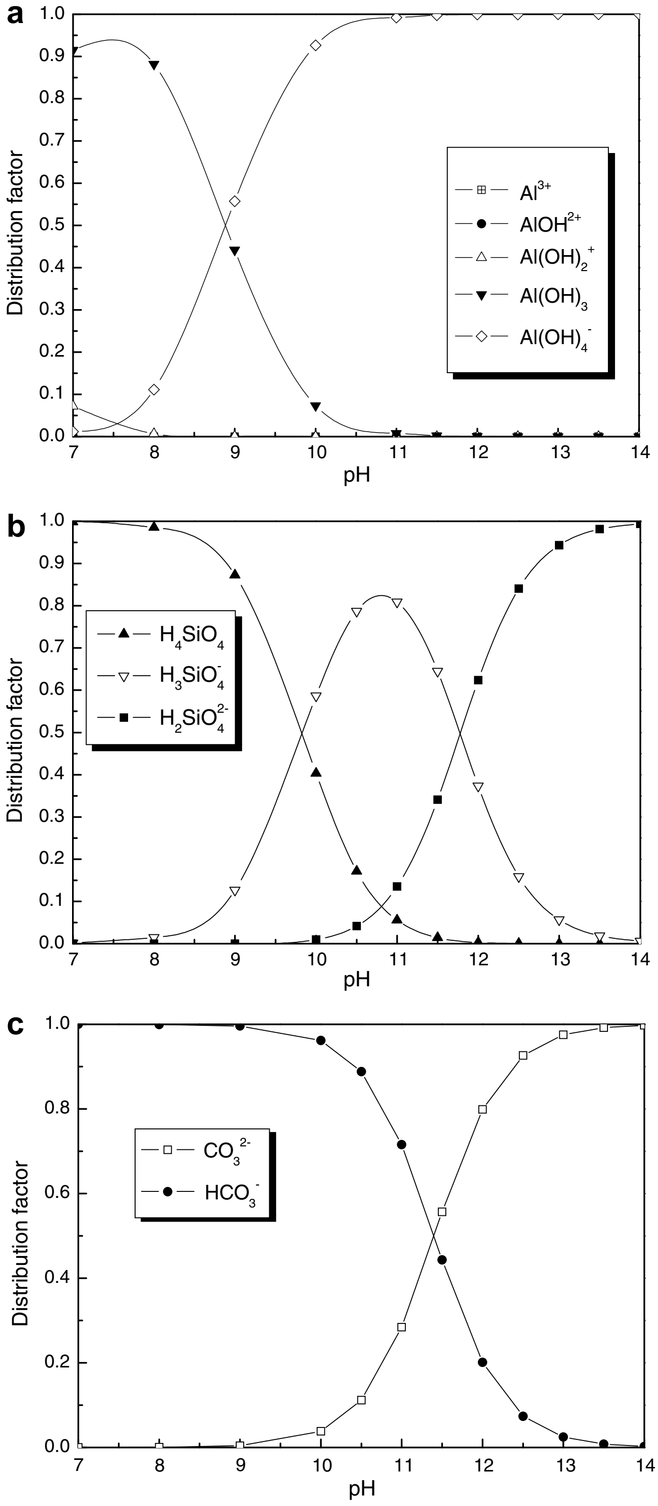

Fig. 1. Distribution factor of aluminum ions, silicate ions and carbonate ions in various form versus the pH at 298 K.

3.2. Relationship between the distribution of silicate ions and the pH

For the silicate ions, such as H_4SiO_4, $H_3SiO_4^-$and $H_2SiO_4^2$, some equilibrium may also be reached according to the following equations:

$$H_4SiO_4 \Longleftrightarrow H_3SiO_4^- + H^+ \tag{9}$$

In Eq. (9), $\Delta G^0_{298} = 56.146$ KJ/mol and $K^0 = 1.456 \times 10^{-10}$.

$$H_3SiO_4^- \Longleftrightarrow H_4SiO_4^{2-} + H^+ \tag{10}$$

In Eq. (10), $\Delta G^0_{298} = 67.221$ KJ/mol and $K^0 = 1.670 \times 10^{-12}$.

Similarly, the distribution factors of H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ can also be calculated, and the result is shown in Fig. 1b.

According to Fig. 1b, when pH > 12, $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are the main forms of silicate ions existing in solution, and distribution factor of $H_3SiO_4^-$ will decrease with increasing pH level, which of $H_2SiO_4^{2-}$ increase? When pH > 13, the main form of silicate ions existing in solution is $H_2SiO_4^{2-}$.

3.3. Relationship between the distribution of carbonate ions and pH

Carbonate ions existing in solution mainly in the form of $CO_3^{2-}$and HCO_3^-, these formations transformed reciprocally as:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \tag{11}$$

In Eq. (11), $\Delta G^0_{298} = 14.835$ KJ/mol and $K^0 = 2.517 \times 10^{-3}$.

Similar calculation is carried out, and the result is shown in Fig. 1c. According to the result, it can be found that when pH > 13, the main form of carbonate ions existing in solution is CO_3^{2-}.

4. Formation of decomposition reactions of alkaline minerals and thermodynamic calculation

4.1. ΔG^0_{298} and K^0 of decomposition reactions of alkaline minerals

In concrete, the decomposition reactions of alkaline minerals occurs under high alkali solution environment with $Ca(OH)_2$ saturation, and pH is often higher than 12. According to the thermodynamic analysis, $Al(OH)_4^-$, $H_2SiO_4^{2-}$ and CO_3^- are the main forms of aluminum ions, silicate ions and carbonate ions exist in solution when pH > 12. So the decomposition reactions of alkaline minerals under pH = 12–14 at 298 K may be described in chemical Eqs. (12)–(20):

Na-feldspar ($NaAlSi_3O_8$):

$$NaAlSi_3O_8 + 2H_2O + 6OH^- \rightarrow Al(OH)_4^- + 3H_2SiO_4^{2-} + Na^+ \tag{12}$$

K-feldspar ($KAlSi_3O_8$):

$$KAlSi_3O_8 + 2H_2O + 6OH^- \rightarrow Al(OH)_4^- + 3H_2SiO_4^{2-} + K^+ \tag{13}$$

Nepheline ($NaAlSiO_4$):

$$NaAlSiO_4 + 2H_2O + 2OH^- \rightarrow Al(OH)_4^- + H_2SiO_4^{2-} + Na^+ \tag{14}$$

Paragonite ($NaAl_2(AlSi_3O_{10})(OH)_2$):

$$NaAl_2(AlSi_3O_{10})(OH)_2 + 8OH^- + 4H_2O \rightarrow Na^+ + 3Al(OH)_4^- + 3H_2SiO_4^{2-} \tag{15}$$

Muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$):

$$KAl_2(AlSi_3O_{10})(OH)_2 + 8OH^- + 4H_2O \rightarrow K^+ + 3Al(OH)_4^- + 3H_2SiO_4^{2-} \tag{16}$$

Jadeite ($NaAlSi_2O_6$):

$$NaAlSi_2O_6 + 4OH^- + 2H_2O \rightarrow Na^+ + Al(OH)_4^- + 2H_2SiO_4^{2-} \tag{17}$$

Dehydration analcime ($NaAlSi_2O_6$):

$$NaAlSi_2O_6 + 4OH^- + 2H_2O \rightarrow Na^+ + Al(OH)_4^- + 2H_2SiO_4^{2-} \tag{18}$$

Dawsonite ($NaAl(CO_3)(OH)_2$):

$$NaAl(CO_3)(OH)_2 + 2OH^- \rightarrow CO_3^{2-} + Al(OH)_4^- + Na^+ \tag{19}$$

Leucite ($KAlSi_2O_6$):

$$KAlSi_2O_6 + 4OH^- + 2H_2O \rightarrow K^+ + Al(OH)_4^- + 2H_2SiO_4^{2-} \tag{20}$$

Using the same calculation method mentioned above, reaction equilibrium constant K^0 and ΔG^0_{298} of these reactions at 289 K could be calculated. The results are listed in Table 2.

It can be seen from Table 2 that the decompositions of alkaline minerals under alkaline conditions are different, and that the one of dawsonite, leucite and nepheline is more serious under normal conditions than others.

4.2. Calculation method

Taking the decomposition reaction of Na-feldspar as example (chemical equation (12)), according to the above reaction mechanism and different distribution of each ion form varying with pH, the K^0 of the decomposition reaction of Na-feldspar can be expressed as follows:

$$K^0 = \alpha_{Na^+} \cdot \alpha_{Al(OH)_4^-} \cdot \alpha^3_{H_2SiO_4^{2-}} / \alpha^6_{OH^-} \tag{21}$$

Table 2
ΔG_{298}, K^0 of decomposition reactions of alkaline minerals at 298 K

Name	Structure formula	ΔG^0_{298} (kJ mol^{-1})	K^0
Na-feldspar	$NaAlSi_3O_8$	−2.533	2.778
K-feldspar	$KAlSi_3O_8$	10.737	1.315×10^{-2}
Nepheline	$NaAlSiO_4$	−71.085	$2.846 \times 10^{+12}$
Dawsonite	$NaAlCO_3(OH)_2$	−83.930	$5.071 \times 10^{+14}$
Dehydration analcime	$NaAlSi_2O_6$	−21.013	$4.802 \times 10^{+3}$
Jadeite	$NaAlSi_2O_6$	12.880	5.545×10^{-3}
Leucite	$KAlSi_2O_6$	−93.610	$2.520 \times 10^{+16}$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	−35.110	$1.416 \times 10^{+6}$
Paragonite	$NaAl_2(AlSi_3O_{10})(OH)_2$	−53.470	$2.338 \times 10^{+9}$

'S_{Na}' (mol/l) represent the maximum amount of Na-feldspar which could take part in the decomposition reaction in alkaline solution, in other words, 'S' represent this part of alkaline mineral which can dissolve in alkaline solution and take part in decomposition reaction. For example, when the decomposition reaction of Na-feldspar attain balance state, there are relationships of ion concentrations between these ions:

$$\begin{array}{l} NaAlSi_3O_8 + 2H_2O + 6OH^- \rightarrow Al(OH)_4^- 3H_2SiO_4^{2-} + Na^+ \\ S_{Na} S_{Na} \cdot \lambda_{Al(OH)_4^-} 3S_{Na} \cdot \lambda_{H_2SiO_4^{2-}} S_{Na} + [Na^+]_0 \end{array}$$

the follow relationship can be deduced:

$$\begin{array}{l} [Na^+] = S_{Na} + [Na^+]_0, \quad [H_2SiO_4^{2-}] = 3S_{Na} \cdot \lambda_{H_2SiO_4^{2-}}, \\ [Al(OH)_4^-] = S_{Na} \cdot \lambda_{Al(OH)_4^-} \alpha_{Na^+} = \gamma_{Na^+}[Na^+], \\ \alpha_{H_2SiO_4^-} = \gamma_{H_3SiO_4^-}[H_2SiO_4^{2-}], \quad \alpha_{Al(OH)_4^-} = \gamma_{Al(OH)_4^-}[Al(OH)_4^-]. \end{array}$$

'γ_{Na^+}', '$\gamma_{H_3SiO_4^-}$', '$\gamma_{Al(OH)_4^-}$' represent the activity coefficient of Na^+, $H_2SiO_4^{2-}$ and $Al(OH)_4^-$, respectively. $[Na^+]_0$ is the concentration of Na^+ from sources other than Na-feldspar. For the concentration of silicate ions and aluminum ions in cement pore solution is lower (usually <0.2 mmol/l) [21,22], the concentration of $H_2SiO_4^{2-}$ and $Al(OH)_4^-$ from sources other than Na-feldspar is ignored in calculation.

Then, the ionic intensity at equilibrium can be written as:

$$\begin{aligned} I &= \frac{1}{2}\sum_i C_i Z_i^2 = 0.5([Na^+] + [Al(OH)_4^-] + 4[H_2SiO_4^{2-}] + [OH^-]) \\ &= 0.5S_{Na}(1 + \lambda_{Al(OH)_4^-} + 3\lambda_{H_2SiO_4^{2-}}) + 0.5[OH^-] \end{aligned} \tag{22}$$

The activity coefficient γ_i of each ion in solution at 298 K could be calculated according to Eq. (4).

According to these equations above, when $[Na]_0$ and the pH value of pore solution are ensured, S_{Na} can be determined, then the maximum content of alkali released from Na-feldspar to pore solution can be calculated.

Similarly, the maximum content of alkali released from other alkaline minerals can also be calculated.

4.3. Influence of pH on the S value of alkaline minerals

Struble [21] has determined by Pressure Filtration Method the components of the pore solution in cements containing different amount of alkali. The results showed that the pH of the pore solution ranged from 13.4 to 14 due to the various cements used, with different alkali contents. Shehata [23] found that the pH level in the pore solution would become lower than 13 when 70% of fly ash was added into concrete. Bérubé et al. [13] suggest that 0.7 N sodium or potassium hydroxide solutions are representative of the pore solution of real concrete (pH ≈ 13.85). For comprehensive study the influence of pH on the S value of alkaline minerals, the decomposition reactions of alkaline minerals occur in alkaline solution with the pH value range from 12 to 14, and alkali ion from sources other than alkaline mineral has no effect on the decomposition reaction (for example, Na-feldspar immerses in KOH solution, K-feldspar immerses in NaOH solution). According to the calculation method mentioned above, S values of alkaline minerals can be calculated. The results are shown in Fig. 2.

According to Fig. 2, when the pH in alkaline solution is higher than 12, the S value of Na-feldspar, K-feldspar, dehydration analcime, paragonite, muscovite and jadeite will increase with increasing pH, while the solubility of nepheline declines slightly with increasing pH slightly; the S value of dawsonite and leucite will drop slightly with increasing pH when pH = 12–12.5, and increase with increasing pH when pH > 12.5. It can be indicated that the S value of alkaline mineral in order is dawsonite > leucite > nepheline > dehydration analcime > paragonite > muscovite > jadeite > Na-feldspar > K-feldspar in alkaline solution with pH > 13.

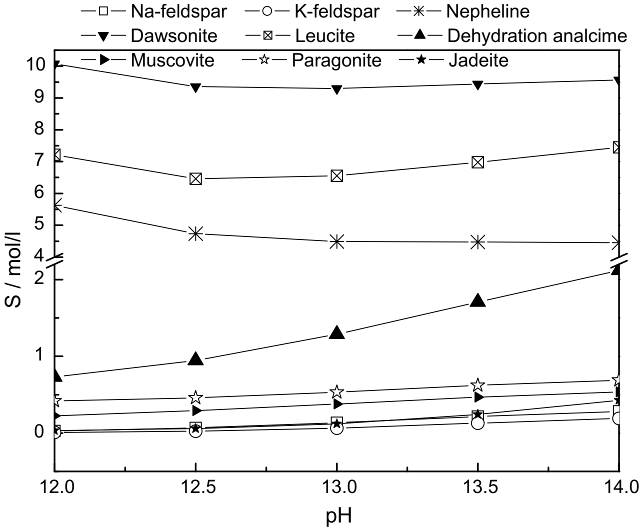

Fig. 2. The S value of alkaline mineral as a function of pH in 298 K.

4.4. Estimation of the maximum alkali released from alkaline minerals

Some tests and calculations have been carried out to determine the S value of alkaline minerals according to the immersion test results in 0.7 mol/l Na^+ or K^+ solutions corresponding to pH ranging from 13 to 14. According to the same method described in 4.2, the calculated results are listed in Table 3.

The amounts of alkalies released from alkaline minerals at pH of 13, 13.5 and 14 were, calculated for 1 m^3 of concrete hypothetically containing 1850 kg of Na-feldspar, K-feldspar, or other alkaline mineral, 367 kg of cement, 183 kg of water ($w/c = 0.5$), and the concentration of Na^+ or K^+ from sources other than alkaline minerals is equal to 0.7 mol/l.

It was noticed that the maximum amount of alkali mineral which could take part in the decomposition reaction in alkaline solution, which is represent with the S value, was ensured in certain pH level in pore solution, thus the amounts of alkalies released from alkaline minerals in concrete only depends on the volume of pore solution (or pore solution/aggregate ratio). A number of experimental procedures have been used in the past to estimate the alkali contribution by aggregates to the concrete pore solution through immersing aggregates in alkaline solution [1–4,13], the ratio of the mass of solution divided by the mass of aggregate, expressed as the solution/aggregate ratio, was used in these tests, the ranges varied from 0.6 to 50. Based on the proportion of aggregate and water mentioned above, the maximum pore solution/aggregate ratio equal to 0.1 (assuming that no water has been bonded in cement and hydration product). Indeed, the pore solution/aggregate ratio in mature concrete is lower than 0.1, for the reason that significant amounts of water have been bonded in cement hydration product. When using low water/cement ratio and lower cement content in normal concrete, the pore solution/aggregate ratio will decrease significantly.

To estimate the effect of pore solution on the alkali released from alkaline minerals, the pore solution/aggregate = 0.05, 2 was adopted, the maximum alkali released

Table 3
The S value of alkaline minerals as a function of pH and initial alkali ions

Name	Structure formula	S (mol/l)					
		$[Na^+]_0 = 0.7$ mol/l			$[K^+]_0 = 0.7$ mol/l		
		pH = 13	pH = 13.5	pH = 14	pH = 13	pH = 13.5	pH = 14
Na-feldspar	$NaAlSi_3O_8$	0.104	0.189	0.258	0.134	0.216	0.282
K-feldspar	$KAlSi_3O_8$	0.064	0.129	0.190	0.038	0.100	0.163
Nepheline	$NaAlSiO_4$	4.470	4.453	4.431	4.491	4.472	4.451
Dawsonite	$NaAl(CO_3)(OH)_2$	9.143	9.289	9.417	9.163	9.309	9.436
Leucite	$KAlSi_2O_6$	6.554	6.978	7.444	6.533	6.959	7.427
Paragonite	$NaAl_2(AlSi_3O_{10})(OH)_2$	0.514	0.605	0.674	0.533	0.621	0.689
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	0.378	0.468	0.536	0.356	0.449	0.519
Dehydration analcime	$KAlSi_2O_6$	1.226	1.655	2.074	1.288	1.707	2.119
Jadeite	$NaAlSi_2O_6$	0.065	0.169	0.350	0.118	0.242	0.428

from alkaline minerals was calculated and the results are listed in Tables 4 and 5.

According to Tables 4 and 5, when the pH value varied from 13 to 14, the maximum alkali released from alkaline minerals increase with increasing pH level excluding nepheline. It can be found that the pore solution/aggregate ratio is the principal factor that influence the maximum alkali released from alkaline minerals. When the pore solution/aggregate ratio increases from 0.05 (Table 5) to 2 (Table 4), the maximum released alkali content increased by 40 times.

From the results listed in Table 5, it can be found that the maximum amount of alkali release depends on the types of alkaline minerals when the pore solution/aggregate ratio is 0.05, which conforms to the order of dawsonite, leucite, nepheline, dehydration analcime, paragonite, muscovite, jadeite, Na-feldspar and K-feldspar; the maximum amount of alkali release range from 0.109 (K-feldspar) to 27.058 (dawsonite) kg Na_2O_e/m^3. The change of pH level in solution have a notable effect on the maximum amounts of alkali released from Na-feldspar, K-feldspar and Jadeite, when pH increases from 13 to 14, the maximum amounts of alkali released from them increase to 2–5 times.

5. Discussion

From the analysis above, the factors that influence the maximum alkali release include the types of alkaline minerals, the pore solution/aggregate ratio, and the type of alkali ions in pore solution from sources other than alkaline minerals. For a certain alkaline mineral, the major factor that influences the maximum alkali release is the pore solution/aggregate ratio, then the pH level in pore solution. The type of alkali ions in pore solution from sources other than alkaline mineral only has insignificant effect. It is suggested that using low water-to-cement ratio and preventing outer water into concrete could effectively reduce alkali released from aggregate.

A number of experimental procedures have been used in the past to estimate the alkali contribution by aggregates to the concrete pore solution [1–4,13]. The test conditions such as the aggregate fineness, the solution used for extraction, the aggregate/solution ratio, the temperature, and the test duration greatly varied from one study to another. However, little attention was paid to the effect of solution/aggregate ratio in the maximum amounts of alkali released. For increasing the rate of alkali leaching, higher water/aggregate ratio was used in these test procedures. The results obtained in long test duration is likely to overestimate the amount of alkali released from aggregate to concrete pore solution in normal concrete.

From calculated results, it was noticed that the effect of pH values in solution on the maximum amounts of alkali release depends on the type of alkaline mineral. The changes of pH level in pore solution have notable influence

Table 4
The calculated maximum alkali released from alkaline minerals in concrete with pore solution/aggregate = 2.0

Name	The maximum alkali released from alkaline minerals (kg Na_2O_e/m^3)					
	$[Na^+]_0 = 0.7$ mol/l			$[K^+]_0 = 0.7$ mol/l		
	pH = 13	pH = 13.5	pH = 14	pH = 13	pH = 13.5	pH = 14
Na-feldspar	11.929	21.678	29.593	15.370	24.775	32.345
K-feldspar	7.341	14.796	21.793	4.359	11.470	18.696
Nepheline	512.709	510.759	508.236	515.118	512.938	510.530
Dawsonite	1048.702	1065.448	1080.130	1050.996	1067.742	1082.309
Leucite	751.744	800.377	853.827	749.335	798.197	851.877
Paragonite	58.956	69.394	77.308	61.135	71.229	79.028
Muscovite	43.357	53.680	61.479	40.833	51.500	59.529
Dehydration analcime	140.622	189.829	237.888	147.734	195.793	243.049
Jadeite	7.456	19.384	40.145	13.535	27.757	49.092

Table 5
The calculated maximum alkali released from alkaline minerals in concrete with pore solution/aggregate = 0.05

Name	The maximum alkali released from alkaline minerals (kg Na_2O_e/m^3)					
	$[Na^+]_0 = 0.7$ mol/l			$[K^+]_0 = 0.7$ mol/l		
	pH = 13	pH = 13.5	pH = 14	pH = 13	pH = 13.5	pH = 14
Na-feldspar	0.298	0.542	0.740	0.384	0.619	0.809
K-feldspar	0.184	0.370	0.545	0.109	0.287	0.467
Nepheline	12.818	12.769	12.706	12.878	12.823	12.763
Dawsonite	26.218	26.636	27.003	26.275	26.694	27.058
Leucite	18.794	20.009	21.346	18.733	19.955	21.297
Paragonite	1.474	1.735	1.933	1.528	1.781	1.976
Muscovite	1.084	1.342	1.537	1.021	1.288	1.488
Dehydration analcime	3.516	4.746	5.947	3.693	4.895	6.076
Jadeite	0.186	0.485	1.004	0.338	0.694	1.227

on alkali released from alkaline minerals excluding dawsonite, leucite and nepheline.

At last, it must be pointed out that the calculated results based on thermodynamic method just apply to decomposition reaction at equilibrium. In normal concrete after long term, a more complete hydration results in the decreasing of the amount of pore solution and the increasing of alkali concentration in pore solution, which decreases the decomposition reaction rate of alkaline mineral in concrete. Indeed, the equilibrium state of decomposition reaction of alkaline mineral in concrete is difficult to attach or requires very long term, thus the calculated results based on thermodynamic method just represent the trend of alkali release from aggregate to pore solution.

6. Conclusion

1. The amount of alkali release depends on the types of aggregates. In alkaline solution with $\mathrm{pH} > 13$, the theoretical maximum alkali released from alkaline minerals are in the order of dawsonite > leucite > nepheline > dehydration analcime > paragonite > muscovite > jadeite > Na-feldspar > K-feldspar.
2. The factors that influence the maximum alkali release include the types of alkaline minerals, the pore solution/aggregate ratio, and the type of alkali ions in pore solution from sources other than alkaline minerals. For certain alkaline mineral, the major factor that influences the maximum alkali release is the pore solution/aggregate ratio, then the pH level in pore solution.
3. The increasing of pH level in pore solution could significantly increase the maximum amounts of alkali released from alkaline minerals excluding dawsonite, leucite and nepheline.
4. Using low water-to-cement ratio and preventing water from entering the concrete could effectively restrain alkali released from aggregate.
5. The test methods used in the past for leaching alkali from aggregate might have overestimated the amount of alkali released from aggregate to concrete pore solution in normal concrete.

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