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Effects of Soak Solution Type on Alkali Release from Volcanic Aggregates – Is Alkali Release Really Responsible for Accelerating ASR Expansion? –

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Abstract
Alkali release from aggregates is considered to cause expansion due to the alkali-silica reaction (ASR), owing to the increase in the hydroxide ion concentration (namely pH) of the pore solution. However, a direct validation of this assertion has not yet been made. In this research, the effects of the type of soak solution, which might better mimic the composition of the pore solution, on the behavior of alkali release from aggregates are investigated through immersion tests of aggregates. More importantly, accompanying ions dissolved from the aggregates are also measured in order to determine the mechanism for the increase in hydroxide ion concentration of the pore solution. The test results show that this increase can barely be observed, despite a considerable amount of alkalis being released. The results critically question the conventional view that alkali released from an aggregate serves to accelerate the ASR.

1. Introduction
Alkali release is a serious concern for long-service structures as it has been noted that an increase in the total alkali content in concrete, due to the alkali-silica reaction (ASR), leads to expansion over a long time period (Durand 2000; Bérubé et al. 2002; Bérubé and Fournier 2004; Sims et al. 2012). Alkali release is a current topic of international discussion, and it is necessary to clarify the risk of alkali release from aggregates and the resulting long-term expansion. Alkali release from minerals has been widely studied in the mineralogical field (Stevens and Carron 1948; Grant 1969; Duddy 1980), while research into cementitious systems began in the late 1970s (Van Aardt and Visser 1977; Grattan-Bellew and Beaudoin 1980; Kawamura et al. 1989; Goguel 1995; Lu et al. 2006).

However, the question of how to evaluate the potential risk of alkali release from aggregates remains controversial. Different tests produce different results and thus it is difficult to interpret the results of testing (e.g., Bérubé and Fournier 2004). The amount of alkali released from an aggregate strongly depends on the particle size of the aggregate, the type of solution, and the solution/solid ratio, as well as the types of minerals that compose the aggregate being tested (Bérubé and Fournier 2004; Lu et al. 2006). In early studies, ground samples were immersed in a saturated lime solution (pH ~12.5) and a significant amount of alkalis was observed to be released (Van Aardt and Visser 1977). It was found that the smaller the particle size, the greater the amount of alkali that was released. The pH value of the pore solution in cementitious materials is around 13.5, owing to the presence of Na⁺ and K⁺, and, as a result, the above method potentially underestimates the potential amount of alkalis released by the aggregate. Increasing the pH of soak solution increases the amount of alkali released from the minerals. The solid/solution ratio used in the test also differs from what is actually present in concrete. Such differences make the problem of alkali release more difficult to understand. The effects of test procedures on the results were reviewed by Bérubé and Fournier (2004). RILEM TC 258-AAA (chaired by Prof. Borge Johannes Wigum) launched work package 3, which is dedicated to establishing a suitable test for the assessment of alkali release from an aggregate as well as from external supplies such as seawater and deicing salt. In most published literature, however, only the amount of alkali released was measured. It should be noted that the hydroxide ion concentration ([OH⁻]), which has a strong impact on pH, is important from the viewpoint of the dissolution of silica minerals. Bérubé and Fournier (2004) hypothesized that, due to the release of alkalis from the aggregates, the lime will supply OH⁻ in order to maintain an equilibrium with the alkali ions, which results in an increase in hydroxide ion concentration. However, although it is the basis for assessing the risk of accelerated ASR expansion, no direct validation of this hypothesis has been made. Constantiner and Diamond (2003) reported that the alkali concentration of a pore solution is increased by the addition of feldspars, but they did not measure hydroxide ion concentration, which is a critical parameter for ASR. Following a publication by

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Bérubé et al. (2002), Tang (2004) and Shi (2004) raised a discussion regarding whether or not alkalis released from aggregates can increase hydroxide ion concentration and thus the pH of the pore solution. Bérubé et al. (2004a, 2004b) argued that this was possible, but did not measure hydroxide ion concentration or pH. They believed that the underlying mechanism was the precipitation of the reaction in the presence of lime. On this basis, it is important to clarify the mechanism of alkali release in terms of increasing hydroxide ion concentration or pH of the pore solution, as well as for ASR expansion. Therefore, measurements taking into account the other ions present would be beneficial in elucidating this mechanism and the risk of accelerated ASR expansion, as these have not been performed thus far.

This research focuses on the release of alkalis, as well as other ionic species such as silicate anions and hydroxide ions, from volcanic rocks collected in Japan. The effects of solution type on the amount of alkali released from the aggregates are also investigated. Based on these results, the potential risk of alkali release from aggregates in terms of accelerated ASR expansion is discussed.

2. Experimental details

2.1 Materials

Sixteen aggregates were collected in Japan. Aggregates classified as andesite or andesitic tuff were used for the tests: fifteen samples from the Noto peninsula and one (B3) from Hokkaido. Each sample was analyzed using X-ray fluorescence, X-ray diffraction, and polarized microscopy. The chemical compositions and mineral compositions of the aggregates are shown in Tables 1 and 2, respectively. These aggregates were classified into three categories: Type A: aggregates without any clay minerals or glass; Type B: aggregates with glass; and Type C: aggregates containing clay minerals.

The samples were ground to have a particle size distribution ranging from 150 to 300 μm in order to avoid large variations in test results. It should be noted that the grinding process would accelerate alkali release.

2.2 Immersion test

The basic test procedures for measuring releasable alkalis used by Bérubé and Fournier (2004) were followed. The ground samples (150-300 μm) were immersed in 1 mol/l NaOH solution to measure the amount of potassium (K), and were immersed in 1 mol/l KOH to measure the amount of sodium (Na). In addition, the effects of the concentration of the alkaline solution were investigated for three aggregates (B1, B2, and C2) in the case of immersion in a NaOH solution for up to 28 days. In order to investigate the effect of calcium, the samples were immersed in a saturated lime solution with an excess amount of solid lime (hereafter, oversaturated lime solution). In the pore solution, the pH can reach 13.6 and an...
excess amount of lime is present in the matrix. In order to simulate this situation, an excess amount of lime was added to the 1 mol/l alkaline solution (NaOH for K, KOH for Na). The aggregate-to-solution ratio was 4 (25 g/100 ml) and the samples were stored in bottles made of polyethylene. Two subsamples were prepared for the test.

The containers were stored in a water bath at 60 °C. During the test, the containers were manually agitated once a day for one month and then twice a week thereafter. The total test duration was 91-182 days. At each testing period, 2 ml of the solutions was sampled via pipette and the same volume of blank solution (1 mol/l NaOH/KOH) was added back to the solutions in order to maintain a constant amount of solution. The collected samples were filtrated and then used for instrumental analysis. The blank solution was prepared using the same procedures as the sampled solutions.

Atomic absorption spectroscopy was used for measuring the amounts of Na and K. First, HC1 was added to neutralize the solution. The solution was highly concentrated which might interfere with the measurement of the target ions. Therefore, NaCl or KC1 was added to the standard solution used for the calibration curve so as to have the same concentration as the original alkaline solution (1 mol/l Na or K for measuring K or Na, respectively). The blank solution was also analyzed using the same procedures. In the case of the oversaturated lime solution, saturated lime solution was added to the standard solution.

The concentration of dissolved silica in the solution was analyzed mainly through photometric analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for supplementary crosschecking. The dissolved silica concentration obtained via photometric analysis was generally 10% and a maximum of 20% higher than that obtained via ICP-AES. This measurement error was relatively large but the measurements are comparable in a qualitative discussion. Therefore, the results obtained via photometric analysis are shown in this paper. The OH− concentration of the blank solution was maintained above 990 mmol/l during testing, such that interference from processes such as carbonation was likely to be limited.

Following these measurements, the amounts of alkalai released were calculated by subtracting the alkali content in the blank solutions and correcting the amount of alkalai removed from the solution for the measurements. Finally, the amounts of released alkali (Na2O/K2O) were calculated as a percentage of the total sample mass.

It should be noted that this proposed method employs some different procedures from that used by Bérubé and Fournier (2004). The laboratory results, however, shows that the variation of the measurement of the alkali was within less than 7.2% on average, and thus the measured values can be regarded as representative of the actual quantity.

3. Results

3.1 Alkali release from aggregates

The amounts of alkalai released from the aggregates in each test solution are presented in Fig. 1 as functions of time. The amounts of released alkali were found to be different for each aggregate type and test solution.

In the pure NaOH solution without lime (Fig. 1(a)), the amount of K released was the largest in Type B (B1-B3), followed by Type C (C1, C2), and finally Type A (A8, A2). The amount of alkali released reached a plateau after 91 days while A6 showed a slight increase at 182 days. The alkali released from the other Type-A aggregates were hardly detected (< 0.05%). In contrast, the trend in the pure KOH solution without lime (Fig 1(b)) was quite different from the case of pure NaOH. Samples C1 and C2 showed large amounts of Na being released soon after immersion. This amount then remained almost constant over the test period. Type-B aggregates showed a small amount of Na being released up to 28 days, followed by a significant increase. Finally, the amount of alkali released from the Type-B aggregates was larger than that in C1 and C2. The Type-A, C3, and C4 aggregates showed smaller amounts of alkali being released (< 0.23%). The amounts of Na released from the Type-A, C3, and C4 aggregates were 1.0 to 6.0 times larger than those of K at 182 days. The ratios of Na to K released for the Type-A, -B, and -C aggregates were 1.0-6.0, 1.5-2.0, and 1.3-3.0, respectively. The largest variations between aggregate types were observed in Type A, but the absolute amount of alkali released from this type was less than that of the other types. When decreasing the concentration of the NaOH solution, as shown in Table 3, the amount of K released was considerably reduced. Therefore, the amount of alkali released strongly depends on the concentration of the alkalai solution, as stated in previous studies (Bérubé and

| Sample | 0.1 mol/l | 0.4 mol/l | 0.7 mol/l | 1.0 mol/l |
|--------|----------|----------|----------|----------|
| B1     | 0.02     | 0.14     | 0.41     | 0.43     |
| B2     | 0.01     | 0.09     | 0.35     | 0.41     |
| C2     | 0.01     | 0.06     | 0.18     | 0.22     |
Some selected aggregates were immersed in an alkaline solution with excess solid lime (Figs 1(c) and (d)). The trends of alkali release of the aggregates were quite similar to those of the samples immersed in an alkaline solution without lime. Even in the presence of excess solid lime, the amount of alkalis released was the largest for Type B, followed by Type C, and then Type A. The amounts of alkalis released at 91 days are compared in Figs. 2(a) and (b). All of the data are located almost on the line of equality, suggesting that lime had little influence on the amount of alkali released by the aggregate.

The immersion test results using the oversaturated lime solution are shown in Figs 1(e) and (f). In this condition, all samples solidified after 1-3 days, possibly

Fig. 1 Alkalis released from the aggregate with time in various alkaline solutions.
due to the formation of reaction products such as calcium (aluminate) silicate hydrate (C-(A-)S-H) (Van Aardt and Visser 1977; Bérubé et al. 2002; Drolet et al. 2017). It was therefore likely insufficient to agitate the sample just once per a day. Consequently, the pH of the solution is likely to be decreased. Therefore, the oversaturated lime solution was considered not to be saturated with respect to portlandite following solidification. The solid phase was not analyzed but its presence might have influenced the results of the tests. The amount of K released in the oversaturated lime solution increased logarithmically with time for each sample but the amount was less than 0.08%. The order of the amounts of alkalis released in the oversaturated lime solution was different from that for the highly alkaline solution. The amount of Na released from B2 was the highest at 91 days, followed by C1 and C2.

The amounts of alkali released are compared in Figs. 2(c) and (d). The amount of K released in the oversaturated lime solution was quite lower (6-32%) than that of the samples immersed in an alkaline solution except for A6 and A9. The amount of K released in the oversaturated lime solution was 15-60% of the amount of Na; a similar trend was observed for the highly alkaline solution. The results for the Type-B samples are located far from the line of equality, which could be attributed to a reduction in the pH of the oversaturated lime solution. Since the dissolution of the glass phase strongly depends on the pH of the solution (Kawabata et al. 2008), it was suppressed as a consequence of insufficient agitation. The ratio of Na to K released ranged from 1.6 to 6.6; a similar trend was observed for the highly alkaline solution. It should be noted that the amounts of K released from A6 and A9 were slightly higher in the oversaturated lime solution. A higher amount of alkalis released in an oversaturated lime solution was also reported by Bérubé et al. (2002) for a few aggregates (shale and pure limestone).

3.2 Other ions

Figures 3(a) and (b) show the amounts of silica released from the aggregates in the pure alkaline solution as a function of time. In the NaOH solution, the amount of dissolved silica was found to be significantly large, even at 7 days. Among the Type-A aggregates, A1 yielded the highest amount of dissolved silica at 7 days, followed by A5, A9, and A4. These aggregates except for A9 contained a large amount of cristobalite (Table 2), which is a
reactive silica mineral known to be susceptible to ASR. Meanwhile, the Type-B aggregates displayed a rapid increase in the amount of dissolved silica at 28 days, but then remained almost constant. Of the Type-C aggregates, C1 and C2 yielded higher dissolved silica at an earlier stage (7-28 days), while C3 and C4 produced amounts of dissolved silica that gradually increased with time. Finally, at 182 days, the dissolved silica contents of all samples ranged from 280 to 960 mmol/l.

In contrast, in the KOH solution, the dissolved silica content was lower than 200 mmol/l at 7 days. No clear distinction can be made between this dissolved silica content and the initial petrographic classification. For most of the aggregates in the KOH solution, the amount of dissolved silica was less than for those immersed in NaOH up to 91 days. Nevertheless, the amount of silica dissolved in KOH at 182 days significantly increased. Interestingly, although the time dependencies are quite different, the final amounts of dissolved silica in the two different alkali solutions at 182 days are similar, as shown in Fig. 4.

Figures 3(c) and (d) show the dissolved silica contents of the samples in the alkaline solution in the presence of excess solid lime as functions of time. These are less than they are for solutions without lime, possibly due to the formation of reaction products, namely C-(A-)S-H. The comparisons of the amounts of dissolved silica for the tested aggregates at 91 days were illustrated in Fig. 5. Figure 5 compares the amounts of dissolved silica for
the tested aggregates at 91 days in alkaline solutions with and without lime; the amounts with excess solid lime are 40-61% in NaOH and 31-80% in KOH of those without lime.

Figure 6 shows the relationships between the amounts of dissolved silica and alkalis released from the aggregates during the testing periods. The plotted data are parallel to the x-axis, meaning that silica was dissolved without any accompanying alkali. Some aggregates, mainly Type-B aggregates, exhibited a positive linear relationship, suggesting that alkali was released with accompanying silica dissolution. The Type-B aggregates...
contain volcanic glass, and K is especially concentrated in the glass phase (Kawabata et al. 2008). Therefore, the source of the alkali can be attributed mainly to the glass phase. The higher amounts of Na released in C1 and C2 can be attributed to ion exchange with interlayer cations by the clay minerals. Even in the presence of lime, the trends were almost the same.

For the oversaturated lime solution, dissolved silica was only measured at 28 and 91 days because of the solidification of the samples. At 28 days, all the samples yielded an amount of dissolved silica less than 1.0 mmol/l. It is reasonable to estimate that the dissolved silica from the aggregate reacted with the Ca ions from portlandite to form C-S-H, resulting in the observed solidification of the samples. At 91 days, however, a considerable amount of dissolved silica was detected, as shown in Fig. 7. Alkalis were also released during this period, such that the dissolution of minerals was sustained during the test period despite the solidification of the sample.

The hydroxide ion concentration of the alkaline solution without lime, as shown in Figs. 8(a) and (b), produced various trends dependent on the aggregate used. Some aggregates exhibited a slight increase in hydroxide ion concentration from 91 days to 182 days (around 50-100 mmol/l), though the hydroxide ion concentrations were less than 970 mmol/l. The relationships between the amounts of released alkali and hydroxide ion concentration are plotted in Figs. 9(a) and (b). Most of the aggregates are located parallel to the y-axis, suggesting the released alkali had no direct influence on the hydroxide ion concentration. Some aggregates, such as B3, also demonstrated a negative quasi-linear relationship, meaning that the hydroxide ion concentration decreased with the increasing amount of alkali released. In the alkaline solution in the presence of excess solid lime (Figs 8(c) and (d)), the hydroxide ion concentrations decreased with time up to 91 days, and exhibited no overall increases with only some temporary increase observed. A similar trend for the relationships between the amounts of released alkali and hydroxide ions was also observed (Figs. 9(c) and (d)).

Figure 10 compares the hydroxide ion concentrations for the tested aggregates at 91 days. Those of the solution with excess solid lime were generally less than those of the solution without lime, typically around 90%, with a maximum of only 101%. Figure 8(c) plots the hydroxide ion concentrations in the oversaturated lime solution. The hydroxide ion concentration of the solution was on the order of 1/10th and decreased with time, because the measurement was inevitably influenced by the solidification of the sample. This solidification is attributed to the formation of C-(A)-S-H, and so the solution was not saturated with respect to calcium hydroxide. Using a oversaturated lime solution would influence test results, so high-frequency agitation is recommended for carrying out tests.

4. Discussion

4.1 Source of alkali release and effect of solution type

From the test results, the susceptibility of minerals from andesitic volcanic rocks to alkali release was estimated. The dissolution of volcanic glass is dominant in alkaline solutions, irrespective of the presence of lime (Fig. 1 (a)-(d)). In contrast, in KOH solutions, the interlayer cations of the clay minerals interact with Na, resulting in their instantaneous alkali release (Fig. 1 (b)). The dissolution of glass in KOH solution then started after 28 days and continued up to 91 days (Fig. 1 (b)). This trend was also observed in the presence of lime (Fig. 1 (d)). The results obtained using the pure alkaline solution agreed well with those found using the alkaline solution with excess solid lime (Fig. 2 (a)-(b)). In the oversaturated lime solution, which would be below saturation after 1-3 days, most of the aggregates yielded lower amounts of alkali released than they would in a highly alkaline solution (Fig. 1 (e)-(f)). The dissolution of glass was also likely to be suppressed under these conditions. Regardless of the type of solution used, Type-A aggregates showed a smaller amount of alkalis being released than the others, although the test duration was relatively shorter than in previous studies (for example, that of Bérubé et al. (2002)). It should also be noted that, from Fig. 11, there is no clear relationship between alkali contents of the aggregates and the amounts of released alkalis.

Differing mechanisms of alkali release from an aggregate may exist, depending on the combination of solution and aggregate. For most of the aggregates tested, it was clear that the amount of alkali released from the aggregates depended on the concentration or pH of the alkaline solution, regardless of the presence of lime. However, some aggregates (A6 and A9,) released almost the same amount of alkali even though the hydroxide ion concentration differed on the order of 1/10th (Fig. 2 (c)-(d)). Similar results were also reported by Soares et al. (2016) and Menéndez et al. (2016). Soares et al. (2016) reported that a higher amount of alkali was released in an
alkaline solution with excess solid lime than in an alkaline solution without lime. Therefore, combinations of solutions and aggregates should be investigated in future work.

4.2 Alkali release and relation to other ions
The experiments conducted in this study highlighted that no direct relationship exists between the amount of alkali released and the hydroxide ion concentration, though a slight increase in hydroxide ion concentration was observed for some aggregates. The behaviors of released K and other ions over time for some selected aggregates are shown in Fig. 12 as typical cases; these were immersed in a 1 M NaOH solution (the results are already shown in

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**Fig. 8** Hydroxide ion concentration in different solutions.
The K-releasing behaviors of A8 and C2 were very similar. After 56 days, the amount of K reached a plateau for both aggregates. Nevertheless, the hydroxide ion concentrations of A8 and C2 increased after 56 days. Simultaneously, the amount of dissolved silica for C2 remained constant over 56-91 days while that of A8 was observed to have decreased. After 91 days, the hydroxide ion concentration of C2 increased along with an increase in dissolved silica. However, the hydroxide ion concentration of A8 decreased slightly within the range of measurement error, despite the fact that the amount of silica had increased. On the one hand, B3 showed a larger amount of K released at 28 days, which then remained almost constant. The amount of dissolved silica was almost constant over 28-91 days and then increased at 182 days for this sample. The hydroxide
ion concentration, however, was observed to have decreased with time. On the other hand, the amount of K released from A9 was significantly lower than for the other samples. The amount of dissolved silica was initially large at 7 days and then gradually increased with time. The hydroxide ion concentration decreased to 910 mmol/l at 7 days but gradually increased after 28 days. The amounts of dissolved silica for samples B3 and A9 were similar after 28 days, though the amount of K released was 15 times higher for B3. Nevertheless, the hydroxide ion concentration of A9 was higher than that of B3. The behaviors of these species are therefore complicated. These results emphasize that measuring only the amount of alkalis in the solution is insufficient when trying to determine the relationship between the amount of alkalis released and the potential risk of long-term ASR expansion.

Bérubé et al. (2004a, 2004b) argued that there is competition between the consumption of alkalis via silica dissolution and the supply of alkalis being released from the aggregate. In fact, it was observed in these experiments that the amount of dissolved silica was higher than that of the alkalis released by one to two orders of magnitude. This therefore makes interpretation of these test results more difficult. The precipitation of the reaction products would also influence the test results. However, no significant increase in hydroxide ion concentration was observed, even though dissolved silica and Ca ions from portlandite were thought to form a considerable amount of reaction products (Fig. 5).

In any case, it can be concluded that not all of the alkalis released are responsible for causing ASR expansion. Further discussion of the interpretation of these test results is therefore required.

4.3 Role of lime

The role played by lime is also worth discussing. Some aggregates yielded the same or higher amounts of alkali released in the oversaturated lime solution, though the amount was below saturation following the reaction, owing to the solidification of the samples. Bérubé et al. (2002) reported that the amount of alkalis released in an oversaturated lime solution was higher than that in an alkaline solution for a number of aggregates. They explained this as being due to the role of lime in the solution. When an oversaturated lime solution is used, lime in the solution would supply hydroxide ions as alkalis are released, resulting in a higher rate of formation of reaction products. However, our experimental results do not support this hypothesis. In the experiments shown in Figs. 2(c) and (d), the amounts of alkalis released from A6 and C3 (and also A9 in NaOH) in the oversaturated lime solution were almost the same as those in the alkaline solution, though there was a difference of more than one order of magnitude in the directly measured hydroxide ion concentration.

![Fig. 11 Alkali contents of aggregate vs. released alkalis (1M NaOH/KOH solution)](image)

![Fig. 12 Comparison of alkali-releasing behavior.](image)
It is also notable that the solution was below saturation with respect to portlandite. In the alkaline solution with excess solid lime, the samples did not solidify because of a lower availability of calcium due to the high pH. Therefore, agitation was carried out effectively, such that Ca ions were considered to be saturated in the solution. As a consequence, the amount of dissolved silica in the alkaline solution with excess solid lime was also 30-80% of that in the pure alkaline solution (Fig. 5). Based on an assumption that the same amount of silica was dissolved, because it strongly depends on the pH of the solution, this means a higher amount of reaction products were formed in the alkaline solution with excess solid lime, suggesting that a large amount of portlandite was consumed for this formation. Nevertheless, the hydroxide ion concentration in the alkaline solution with excess solid lime was almost the same as that in the pure alkaline solution, despite the higher amount of dissolved silica that was consumed for C-S-H formation. It is widely believed that alkali release from the aggregate mainly depends on the pH of the solution. Most of the tested aggregates agreed with this assertion; however, other possible mechanisms should be considered.

Wang et al. (2008a) proposed another mechanism, namely that the amount of alkalis released from an aggregate mainly depends on an ion exchange between the surface layer of the minerals and the Ca ions in solution. According to the results of the present research using alkaline solutions with and without lime, however, there is no evidence to support this theory.

### 4.4 Potential risk of alkali release from aggregates causing the alkali-silica reaction

The above discussions focused heavily on the mechanism of alkali release from the aggregates. The mechanism for an increase in pH caused by alkali release from the aggregates is discussed in detail here. Menéndez et al. (2016) reported that alkali release in ultrapure water increased pH. This phenomenon, however, is well known in the field of geochemistry as the so-called abrasion pH, which occurs when a mineral is ground in water and the pH of the water is increased by alkalis released from the mineral (Stevens and Carron 1948; Grant 1969; Duddy 1980). This reaction is mainly a hydrolysis reaction.

According to the current experiments, however, it is questionable whether the release of alkali from the aggregate does indeed directly increase the hydroxide ion concentration of the solution. Incongruent dissolution of minerals might increase the alkali concentration of the solution. According to the results, however, most alkalis were likely to be released with an accompanying dissolution of silicate anions or other ions. In this case, there is no direct increase in pH caused by alkali release. An approach using thermodynamic modeling by Wang et al. (2008b) showed that [OH⁻] is consumed rather than supplied.

It has been proposed that pH would be increased by consuming portlandite, as a result of the formation of reaction products: hydroxide ions would be supplied to the pore solution by consuming Ca ions from portlandite for the reaction (Bérubé and Fournier 2004). As described above, however, the apparent increase in hydroxide ion concentration was not observed, even in the presence of lime.

It may be claimed that the immersion test is quite different from a realistic pore solution in mortar or concrete. In the immersion test, the role of lime might be weakened by the higher pH of the solution and higher the liquid/solid ratio. In addition, the reaction occurring in concrete is slower in practice, such that ion exchange of the ASR gel with Ca ions mainly coming from portlandite occurs. However, considering that the reaction between silicate and Ca ions from portlandite would mainly form C-S-H, and that the Ca/Si ratio of C-(A-)S-H cannot become any higher in a highly alkali solution because of the competition between alkali and Ca ions, a certain amount of alkali uptake by C-S-H should take place (Hong and Glasser 1999, 2002; Kawabata and Yamada 2015). In fact, a considerable amount of silicate anions remained in the pore solution. Table 4 shows the chemical composition of a pore solution extracted from a mortar affected by ASR (with andesite as the reactive aggregate) (Kawabata et al. 2007). A higher amount of Si was detected for the mortar exhibiting greater expansion.

These results contradict the hypothesis of an increase in hydroxide ion concentration or pH being caused by alkali release in the presence of lime.

These results indicate that a large gap should exist between the amount of alkali released in the immersion test and the potential risk of increased hydroxide ion concentration in concrete. Drolet et al. (2017), for instance, investigated the actual alkali contribution by aggregates to a pore solution by means of high-pressure pore solution extraction and other techniques. The amount of alkali released was then compared to the amount of releasable alkali in an immersion test. They concluded that the amount of releasable alkali measured by the immersion test overestimated the realistic amount of alkali released in concrete or mortar specimens. This result reveals a potential link between laboratory and field testing, but the important point is how these alkalis released from the aggregate increased hydroxide ion concentration and thus accelerated or sustained expan-
sion due to ASR.

Durand (2000) conducted concrete prism tests that indicated that the expansion of concrete was possibly accelerated by the alkali released from aggregates (nepheline syenite), the amount of alkali released or the actual hydroxide ion concentration was not measured. Therefore, it would be premature to conclude that the alkali released from aggregate directly accelerates the expansion due to ASR. This research and the previous studies on pore solution composition (Table 4) critically call into question the assertion that alkali metal ions are always counterbalanced by hydroxide ions. Therefore, measuring only alkali metal ions is insufficient and thus it is strongly suggested that that measurement of other ions also be performed, in order to discuss the “realistic” potential risk of alkali release in sustaining long-term ASR expansion.

5. Conclusions

This paper investigated the effects of the type and concentration of a solution on alkali release from an aggregate, while also examining the behavior of accompanying ions such as silicate and hydroxide ions. The potential risk of alkali release in terms of increasing the hydroxide ion concentration was then discussed. The main conclusions are summarized as follows:

(1) The amount of alkali released from aggregates depends on the concentration of the alkaline solution regardless of the presence of lime, while some aggregates exhibited a slightly higher amount of alkali released in the oversaturated lime solution. The higher the concentration of the alkaline solution, the higher the observed amount of alkali released.

(2) Dissolved silica remained considerably high even in the alkaline solution with excess solid lime. In the presence of lime, the amount of silicate anions decreased, which indicates the precipitation of the reaction products, namely silicate anions and Ca ions.

(3) The hydroxide ion concentration in the alkaline solution with excess solid lime was lower than that in a pure alkaline solution for most of the aggregates, even though a higher amount of reaction products was thought to be formed in the alkaline solution with excess solid lime. Regardless of the presence of lime, no considerable increase in hydroxide ion concentration was observed.

(4) From the results of immersion tests with various concentrations, no evidence was found that alkali release from the aggregate serves to increase the hydroxide ion concentration of the pore solution, with reference to previous studies on high-pressure pore solution extraction. These results strongly suggest that it is necessary to consider the mechanism of alkali release and its risk of causing expansion induced by the alkali-silica reaction.

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