Pergamon

Cement and Concrete Research 33 (2003) 549–554

CEMENT AND CONCRETE RESEARCH

Alkali release from feldspars into pore solutions

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Received 8 May 2002; accepted 19 September 2002

Abstract

For many years, the possibility that alkalis may be released from feldspars and other alkali-bearing aggregate components directly into concrete pore solutions has been explored by various mostly indirect methods. In this study, we demonstrate this effect unambiguously by direct measurements of the concentrations of alkalis in pore solutions expressed from mortars with and without such aggregates. Mortars with three different alkali-bearing feldspar minerals all released significant amounts of alkali ions. This evidence confirms the indications provided by others who monitored the release of alkalis into external solutions of calcium hydroxide or alkali hydroxide. It was also found that when both feldspar and a reactive aggregate (calcined flint) were present, some of the released alkali ions were taken up into ASR reaction products. These findings lend further emphasis to the likely importance of alkali release in many practical ASR problems.

Keywords: Alkali aggregate reactions; Alkali release; Pore solution; Feldspars

1. Introduction

The possibility that certain aggregate components release alkalis directly into concrete pore solution has been considered for many years. Such alkali release from aggregates could enable ASR to occur even with low alkali cements. A considerable number of studies have reported the results of investigations of this possibility.

In many of these studies, alkali release was studied from crushed aggregates shaken or stirred in various solutions, most commonly saturated calcium hydroxide solutions. Van Aardt and Visser [1–3] described studies in which slurries containing crushed aggregate, calcium hydroxide (CH), and water were stored in sealed containers at various temperatures. Significant proportions of the total alkalis in the aggregate were released into the CH solution, especially at higher temperatures. It was found that the alkali-releasing aggregates often reacted to form new crystalline phases. Way and Cole [4] showed that, at 50 °C, certain finely crushed aggregates released significant amounts of alkalis in CH-saturated solutions. They found that coarsely ground fractions of the same rocks released much less alkali. Many of the aggregates employed in these leaching studies contained alkali feldspars, which have long been suspected of being a primary source of releasable alkalis. Stark and Bhatty [5] documented that feldspar-containing American aggregates released significant amounts of alkali into saturated CH solutions at 38 and 80 °C; similarly, Jensen [6] found that a number of feldspar-bearing Norwegian aggregates released alkalis into saturated CH solutions at 40 °C.

Saturated solutions of CH have a pH level of the order of 12.5 (depending on temperature). Concrete pore solutions often have much higher pH levels, sometimes reaching pH levels in excess of 13.8. Thus, measurements of the release of alkalis into saturated CH solutions may underestimate the potential amount of alkali release. In extensive comparative studies, Berubé et al. [7,8] found that this was indeed the case. Sand-sized crushed aggregates, especially feldspar-bearing ones, were found to release significantly greater amounts of alkalis into 0.7 M alkali hydroxide solutions than into saturated CH solutions under identical conditions. On the other hand, Constantiner [9] found that, in agitated suspensions, increasing the KOH concentrations of solutions saturated with CH had little effect on the release of alkali from Na-feldspar.

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0008-8846/02/$ – see front matter
PII: S0008-8846(02)01001-3

Leaching studies such as those referred to above have shown clearly that feldspars and certain other alkali-bearing aggregate components can readily release alkalis into *external* solutions. However, such studies usually involve prolonged agitation of small amounts of aggregate suspended in relatively large amounts of solution, a very different environment than the static and more constrained environments of the solutions within the pores of mortars or concretes. A number of workers have attempted to show indirectly that such release can take place within concretes, either in laboratory studies or in field investigations. For example, Poulsen et al. [10] found that substituting feldspar for inert quartz aggregate in mortar bars significantly increased the pessimum proportion of reactive chert aggregate undergoing ASR, and produced much higher expansions. With respect to field concretes, Berubé et al. [11] used a hot water extraction method to remove so-called "soluble" alkali from concretes sampled from concrete dams in Canada. The soluble alkali contents found "often largely exceed the water-soluble alkali content expected to be released by the cement..., often by more than 1 kg/m^3 Na_2O_{eq}". The amount of excess alkali found was particularly large when feldspar-rich aggregates were present.

Indirect but convincing evidence that the alkali released from feldspar-bearing aggregates in concrete had significantly enhanced ASR reactions in field concrete has been found by several authors. For example, Shayan [12] found such effects in his investigation of the cracking of concrete railway ties made with gneissic granite aggregates in Australia.

It is possible to obtain direct and absolute evidence for alkali release from feldspars and other rock in concrete or mortar by expressing and analyzing pore solutions from specimens made with such aggregates, and noting the excess of alkali found compared with the alkali found with companion specimens made with inert alkali-free aggregates. Experiments of this kind were carried out by Kawamura et al. [13], who measured OH^- ion concentrations in pore solutions expressed from mortars containing alkali-bearing andesite rock. Two types of andesite aggregate were investigated. Both contained significant amounts of feldspars (and other possible sources of alkali), and both were strongly ASR reactive. When tested by exposure to saturated CH solution, both types of rock were found to release alkali. However, in pore solutions expressed from mortars containing these aggregates, the OH^- ion concentrations measured were less than those of counterpart mortars containing only quartz.

In the present work, we provide (1) direct evidence that feldspar minerals constrained in mortars will in fact release significant amounts of alkali ions to the pore solution and (2) that some of the released alkalis can be subsequently removed from solution when ASR-reactive aggregate components are also present.

2. Materials and experimental procedures

A series of mortars was prepared using a very low alkali ASTM Type I white cement. This cement was chosen to minimize the alkali concentration supplied by the cement to the pore solution, thus facilitating the assessment of changes induced by release of alkali from aggregates. The mill analysis provided by the manufacturer indicated the following cement composition: CaO: 70.03%, SiO_2: 23.88%, Al_2O_3: 1.94%, Fe_2O_3: 0.43%, MgO: 0.0%, K_2O: 0.02%, Na_2O: 0.10%, SO_3: 1.82%. Note that the small amount of alkali present in this cement was primarily as Na_2O, with almost no K_2O present. The cement had a Blaine fineness of 405 m^2/kg.

The inert alkali-free aggregate used in the mortars was an almost pure calcitic limestone; its X-ray diffraction pattern indicated only traces of dolomite and quartz impurities.

Two different series of mortars were prepared. In the first portion of this work, designed to study alkali release without the complication of simultaneous ASR, ground feldspars of several different types were incorporated into the mortars as partial replacement for the limestone. Three different feldspar types were obtained as mineral specimens[1]: microcline (a K-rich feldspar) oligoclase (a Na-rich feldspar) and labradorite (a feldspar containing significant contents of both alkalis). Representative portions of these mineral samples were hand-separated from visible contaminants, crushed, and their alkali contents determined by chemical analysis after lithium metaborate fusion. The alkali contents found were as follows: microcline: 11.2% K_2O, 2.65% Na_2O; oligoclase: 0.74% K_2O, 8.6% Na_2O; labradorite: 1.57% K_2O, 5.81% Na_2O.

To facilitate alkali release within the mortars, only particles passing the No. 400 sieve (<36 μm) were incorporated. The surface areas of these sieved fractions were determined by N_2 absorption, and were found to be 720, 610, and 860 m^2/kg for the microcline, oligoclase, and labradorite, respectively.

To avoid potential differences in water demand between mortars of different levels of feldspar replacement, the inert limestone used as the primary aggregate component in the first series of mortars was also ground to pass the No. 400 sieve. In these mortars, the total aggregate to cement ratio was maintained at a constant level of 1.0, and the water to cement ratio was 0.65 throughout. The relatively high water to cement ratio was necessitated by the high water demand induced by the fineness of the aggregates. The feldspars were incorporated at replacement levels of 20% and 40% by mass.

In a second part of this study, mortars that were more nearly similar to the standard mortars commonly used in ASR mortar bar testing were prepared. For these mortars,

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[1] Obtained from Ward's Natural Science Establishment, Rochester, NY, USA.

the limestone aggregate was graded into the five size classes specified in ASTM C 227 and combined in equal parts. For these mortars, the aggregate to cement ratio was 2.25, and a constant water to cement ratio of 0.65 was used.

Only one feldspar was used in the second part of the study; this was the ground microcline used in the first series of experiments. Only a single replacement level of 25% was used. To keep a consistent water demand, in the control mortar in this series, 25% of each of the graded limestone aggregate size fractions was replaced by the finely ground limestone previously mentioned.

In addition to the feldspar-bearing mortar and the control mortar containing only inert limestone aggregate, two other mortars were prepared, both containing ASR reactive aggregate. The reactive aggregate was calcined flint,[2] an ASR reactive aggregate commonly used in experimental studies. The replacement level of this calcined flint was fixed at 30%, the pessimum proportion for this aggregate as determined by Struble and Brockman [14]. One of these mortars contained only the calcined flint as a chemically active component; the other contained both the calcined flint and the microcline feldspar.

All of the mortars were mixed in accordance with the standard mortar mixing procedure outlined in ASTM C 305, and placed in plastic ointment jars suitable for subsequent removal and pore solution expression. These were immediately sealed and maintained at 38 °C for various periods, after which pore solutions were expressed and analyzed according to the procedures outlined by Barneyback and Diamond [15].

3. Results: release of alkalis from different feldspars

As indicated previously, the first part of this study was designed to directly measure augmentation of pore solution alkali contents by each of three different types of feldspar.

The control mortar, prepared without feldspar or other alkali-bearing aggregate, was used to establish the basis for the unaugmented alkali concentration level. Microcline and oligoclase-bearing mortars were prepared at 20% and 40% replacement levels; for the labradorite-bearing mortar, only the 40% replacement level was employed.

Pore solutions were expressed from each of these mortars at ages of 1, 2, and 4 months, and analyzed for the concentrations of the alkalis. The results are given in Table 1.

As expected from the low alkali content of the host cement, the concentrations of the alkali ions in the pore solutions of the control specimens were low; also as expected, Na^+ ions constituted the bulk of the alkali found in solution. The alkali concentrations increased very slightly over the 4-month period studied, the increase being likely due to reduction in content of the solvent water as the cement continued to hydrate. It should be recalled that the mortars were in sealed containers without access to external water.

Table 1
Alkali ion concentrations (mol/l) in pore solutions expressed from mortars with and without ground feldspars

Age (months)	Control (no feldspar)	Microline		Oligoclase		Labradorite	
		20%	40%	20%	40%	–	40%
Na^+ ion concentrations							
1	0.079	0.078	0.082	0.098	0.112	–	0.107
2	0.078	0.081	0.083	0.113	0.140	–	0.130
4	0.085	0.088	0.092	0.152	0.183	–	0.169
K^+ ion concentrations							
1	0.009	0.024	0.034	0.009	0.009	–	0.014
2	0.009	0.028	0.043	0.011	0.011	–	0.017
4	0.013	0.042	0.064	0.016	0.015	–	0.021

The results for the microcline-bearing mortars given in Table 1 show the effects of substantial alkali release from this feldspar. The alkali released from the microcline feldspar was primarily (but not entirely) in the form of K^+ ions, as expected from the composition of this feldspar. The alkali concentrations increased substantially over time, obviously due to continued release from the feldspar. The 40% replacement mortars show somewhat greater release at any given age than the corresponding 20% replacement mortars.

For the oligoclase-bearing mortar, Table 1 shows that the augmentation is primarily as Na^+ ions from this mostly Na-bearing feldspar. The 40% replacement mortars yielded significantly higher Na^+ ion concentrations at each age than the 20% replacement mortars.

The single labradorite-bearing mortar examined (at 40% replacement) showed a time trend similar to that of the corresponding oligoclase-bearing mortar, but here some K^+ augmentation was found in addition to the much more significant Na^+ augmentation.

An assessment of the total alkali release versus time for the various feldspar-bearing mortars is provided in Fig. 1. In this figure, we plot the excess concentration of combined K^+ and Na^+ ions at each age, after subtracting the alkali concentration found in the control mortar at the same age. This excess concentration is a direct measure of the alkali released from the feldspars. A reasonably linear rate of increase in net excess alkali concentration was observed after the first month for the two 20% replacement mortars and for the 40% replacement with microcline, suggesting that a steady rate of alkali release had been established for these mortars and maintained during the period of testing.

It is seen in Fig. 1 that the slopes of the lines, representing the rates of alkali release, are generally higher for the 40% feldspar mortars than for the corresponding 20% feldspar mortars, but less than proportionately so.

These data offer direct evidence that the alkali content in the pore solution can be significantly increased by partial

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[2] Supplied by Blue Circle Industries, London, UK.

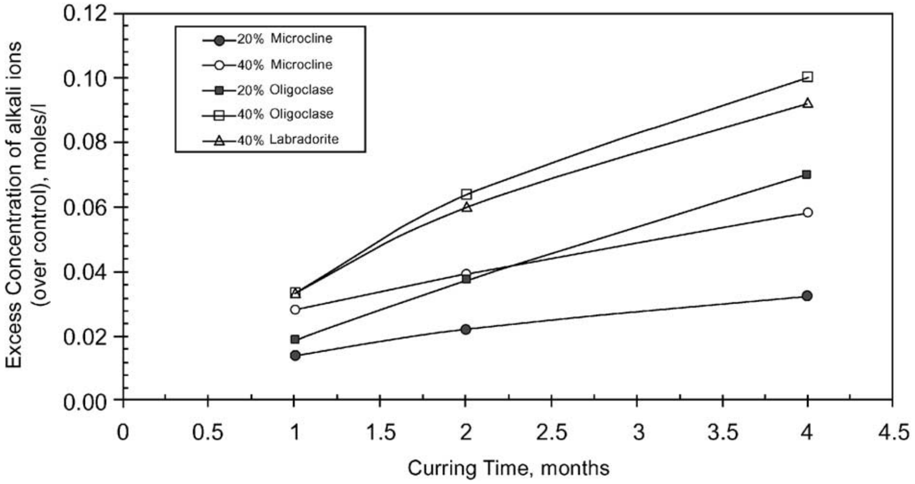

Fig. 1. Net increase in combined alkali ion concentrations in pore solutions expressed from feldspar-bearing mortars (as compared to control mortars without feldspar at the same ages).

dissolution or reaction of the aggregate when alkali-bearing aggregates (specifically feldspars) are embedded in a cement matrix.

4. Results: alkali release and ASR

As mentioned above, a second set of four experimental mortars containing a reactive aggregate were prepared to investigate whether the alkalis released by feldspars could be shown to actively participate in ASR. The compositions of these mortars have been previously described. For these mortars, pore solutions were expressed and analyzed after continuous storage in sealed containers at 38 °C for 2, 4, 6, and 10 months. Expressed pore solution concentrations of Na^+ and K^+ ions at these ages are given in Table 2. Fig. 2 provides plots of combined alkali contents vs. time.

The plot for the limestone-only mortar (containing no feldspar and no calcined flint) is bold in Fig. 2 to show the base level of concentration of the combined alkalis in these mortars; the data are shown as filled circles. This plot constitutes the 'base line' from which other effects are measured. As shown in Table 2, most of the alkalis are Na^+, with only a little K^+. The combined alkali concentration hardly changes over time; the modest increase reflects the fact that only a little additional hydration has taken place between 2 and 10 months.

The first effect to which attention is called is the augmented alkali concentration level for the microcline feldspar-containing mortar, shown as open square markers in Fig. 2. At 2 months, the total alkali ion concentration here was about 50% higher than the base level in the control mortar. As seen in Fig. 2, the feldspar continued to release alkalis between 2 and 10 months, the alkali ion concentration at 10 months reaching 0.270 M. This is a significant contribution to the alkali concentration, which has become sufficiently high to raise the possibility of potential ASR activity. As seen in Table 2, the augmentation between 2 and 10 months was mostly, but not entirely, as K^+ ions.

The corresponding results for the mortar containing 30% ASR-reactive calcined flint (but no feldspar) are shown as open diamond markers in Fig. 2. This mortar was prepared to study the effect of ASR in reducing the alkali ion concentrations. Thus the effect expected is the reverse of the effect of alkali release from the feldspar. It is evident that such activity did occur. The combined alkali concentration at 2 months in this mortar was significantly *less* than that found in the control mortar, indicating that some of the alkali (mainly Na^+) had reacted with the calcined flint. Further exposure produced additional modest reduction. Thus, despite the low base level of alkali concentration resulting from the use of a low-alkali cement, some of the alkali ions were progressively removed from the pore solution by reaction with the calcined flint. The amount of

Table 2
Alkali ion concentrations (mol/l) in pore solutions expressed from various mortars prepared to study the effects of alkali release by microline feldspar on ASR

Age (months)	Na^+				K^+			
	2	4	6	10	2	4	6	10
Control mortar (without added reactive components)	0.104	0.108	0.111	0.110	0.013	0.010	0.012	0.020
Mortar containing 30% calcined flint (ASR reactive component)	0.093	0.091	0.087	0.085	0.010	0.009	0.010	0.012
Mortar containing 25% microline feldspar	0.120	0.126	0.133	0.146	0.057	0.077	0.092	0.124
Mortar containing 30% calcined flint and 25% microline feldspar	0.096	0.098	0.098	0.099	0.049	0.060	0.065	0.078

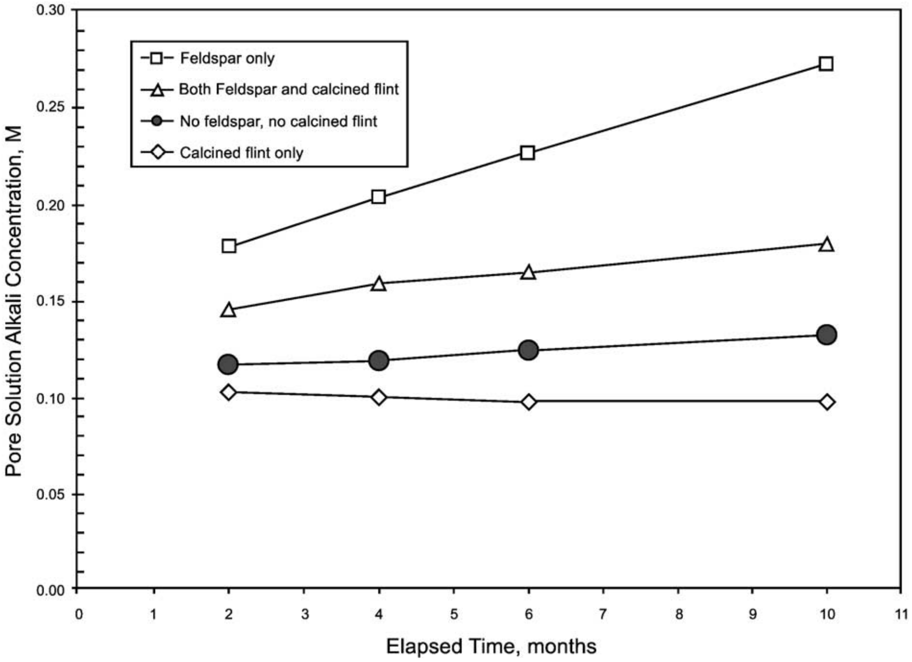

Fig. 2. Alkali ion concentrations found in pore solutions expressed from various mortars prepared to study the effects of alkali release by microcline feldspar on ASR.

ASR gel formed was insufficient to cause noticeable distress.

Finally, a combination of the two separate effects was observed for the mortar containing both the microcline feldspar and the ASR reactive calcined flint, shown as open triangle markers in Fig. 2. At 2 months, the combined alkali ion concentration for this mortar, 0.135 M, was significantly greater than that of the control mortar, and of course of the mortar containing only reactive aggregate. It is apparent that the release of alkali from the feldspar outweighed the removal of alkali by reaction with the calcined flint. As seen in Table 2, the Na^+ concentration remained approximately constant over time, i.e., the rate of Na^+ release from the feldspar appeared to match the rate of Na^+ uptake by the reactive aggregate. On the other hand, in spite of some removal of K^+ by ASR, there was a progressive increase in concentration of K^+ ions with time. Apparently, the rate of K^+ release by the microcline feldspar was faster than the rate of K^+ consumption by the calcined flint reactive aggregate.

If one assumes that alkali release by the microcline feldspar and alkali removal by the reactive aggregate are completely independent processes, it is possible to calculate the proportion of the feldspar-derived alkalis taken up by the reactive aggregate. The release of alkalis from the feldspar at each age is taken as the difference between the concentrations found in the feldspar-bearing mortar and the control mortar. The uptake of alkali by the calcined flint at each age is taken as the difference between the concentrations found in the feldspar-bearing mortar and the mortar with both feldspar and calcined flint components. The uptake divided by the release provides an estimate of the portion of the feldspar-derived alkali that is removed from solution by the ongoing ASR reaction. The values obtained by this calculation suggest that between one-third and one-half of the alkali ions released by the feldspar were removed from the pore solution by the ASR reaction.

5. Discussion

The data presented here provide definitive evidence that feldspars incorporated in concrete or mortar indeed release alkalis to the pore solution, despite the restricted solution mobility that prevails within the pores. The K-feldspar (microcline) is seen to contribute *primarily* K^+ ions to the pore solution; the Na-feldspar (plagioclase) is seen to contribute *primarily* Na^+ ions, and the oligoclase feldspar, with significant contents of both alkalis, contributes both.

The release of alkali from the feldspars is, of course, a time-dependent process. As seen for the plot of the "feldspar-only" mortar in Fig. 2, even at 9 months, there is no falling off in the rate of alkali release, suggesting that the process is continuing. This is in spite of the fact that the feldspar used was relatively finely ground. The implication is that alkali release in field concrete is likely to be a slower, but prolonged affair.

A source of confusion can arise in experiments if the alkali-releasing aggregate is also ASR reactive, or else if other ASR-reactive components are also present. The release of alkali ions from aggregate into the pore solution may be masked by uptake of alkali ions from the pore solution into ASR reaction products. If the alkali-bearing rock is itself ASR reactive, the two processes are necessarily confounded.

This confounding arose in the experiments carried out by Kawamura et al. [13], who measured OH^- ion concentrations in pore solutions expressed from mortars containing alkali-bearing andesite rock. When tested by exposure to saturated CH solution, both types of rock (containing feldspars) were found to release alkali but both were strongly ASR reactive. In pore solutions expressed from mortars containing these aggregates, the OH^- ion concentrations measured were actually less than those of companion mortars containing only quartz. It appeared that alkali release likely took place in the mortars, but the effect was overbalanced by the removal of alkali from the pore solution into ASR reaction products.

The work of Van Aardt and Visser [1–3] indicated that alkali release from feldspars in dissolution studies in saturated CH solution involves chemical reaction rather than simple dissolution. No evidence is provided in the present experiments, as to the details of the process of alkali release within concretes. Because of the obvious practical consequences of such alkali release in concretes subject to ASR, a detailed physical–chemical and microstructural study of the alkali-releasing process would certainly be warranted.

Finally, the demonstration that a significant portion of the alkali released from feldspar can be taken up by ASR reactive aggregates confirms that the release of alkali from aggregates in field concretes may be of importance in many practical ASR problems, especially where low alkali cements have been used in the expectation that such use would prevent ASR. In fact, Shayan [16] has investigated a major bridge structure in which an alkali releasing basalt aggregate (containing labradorite feldspar) was used in the form of coarse aggregate as well as “crusher dust.” In one section of the bridge, a nonreactive sand was used and no ASR problem occurred. In another section the sand component was ASR-reactive. All other factors were the same, including the use of low alkali cement. Despite the use of low alkali cement, the second section developed ASR damage due to alkali release from the basalt dust into the concrete pore solution, which enabled the reactive sand to produce deleterious expansion and cracking.

6. Conclusions

Direct measurement of alkali concentrations in pore solutions expressed from mortars with and without feldspars of several kinds show that: (1) feldspars (and presumably other alkali rich aggregates) embedded in a cement matrix do release alkali ions into the pore solution and (2) that, if ASR-reactive aggregates are present, these released alkali ions can participate actively in ASR.

Acknowledgements

The research reported here was carried out at Purdue University and constituted a portion of the PhD thesis of the first author [9].

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