

IMMERSION TEST TO IDENTIFY CEMENT ALKALI LEVELS AND POZZOLANS TO PREVENT ASR

D. C. Stark
Materials Research and Consulting Group
Construction Technology Laboratories, Inc.
5420 Old Orchard Road
Skokie, Illinois, 60077-1030
U.S.A.

ABSTRACT

ASTM C 227 (mortar-bar), ASTM C 289 (quick chemical), and ASTM C 1260 (rapid immersion) tests are either too lenient or too severe, and do not permit determining the minimum requirements for safe cement alkali levels or pozzolans for specific field installations. Experimental work in the Strategic Highway Research Program (SHRP), conducted in the United States during 1988 to 1993, indicated that the C 1260 procedure, adapted from that developed by Oberholster and Davies in South Africa, lends itself to identifying these requirements using certain modifications. This includes adjusting the molarity of the sodium hydroxide immersion solution to correspond to specific cement alkali levels and water-cement ratios, and making adjustments in the failure criterion. Based on a comprehensive literature review, an equation was developed to calculate the appropriate solution molarity for a given cement alkali level. Based on field performance, a projected adjustment of the failure criterion was made. This use of the procedure is still under refinement and evaluation. Test data are provided to illustrate the application of this approach to preventing expansive alkali-silica reactivity in concrete.

Keywords: alkali-silica reactivity test, cement alkali level, fly ash

INTRODUCTION

A primary objective of tests to identify susceptibility to expansive alkali-silica reactivity (ASR) is the selection of innocuous cement-aggregate combinations for field use. Predictions based on current long-standing ASTM tests have been found, in many field installations, to be erroneous, particularly for so-called slowly reacting aggregates and the use of low alkali portland cements (alkali contents less than 0.60% as equivalent Na_2O). In general, these tests have been too lenient. The development of the rapid immersion test at the National Building Research Institute (NBRI) in South Africa (Oberholster and Davies, 1986) has become widely accepted as a rapid and more appropriate test, and has been adopted in slightly modified form as ASTM C 1260, "Standard Test for the Rapid Identification of Alkali-Reactive Aggregates (Mortar Bar Method)." As it now stands, the test appears to be too severe in that it may identify an aggregate to be potentially deleteriously reactive while, in field structures, it has performed satisfactorily for many years even with the use of high alkali cements. With some modifications, it appears that the procedure could identify safe cement alkali levels more in accordance with field performance, and also identify the requirements of mineral admixtures to prevent deleterious ASR. Details of these modifications, and experimental results are presented below.

EXPERIMENT BASIS

It is generally agreed that higher cement alkali levels lead to earlier and more severe ASR and attendant distress due to expansion in a given exposure environment than lower alkali levels. The importance of cement alkali level lies in the resulting alkalinity of the pore solution in the concrete. In a review of the published literature, a linear regression equation was developed that related hydroxyl ion solution molarity to cement alkali level for different water-cement ratios (Helmuth, 1993), as follows:

$$[\text{OH}^-] = 0.339 \frac{\text{Na}_2\text{O}}{\text{w/c}} + 0.022 \pm 0.06 \text{ moles/liter} \quad (1)$$

where:

$[\text{OH}^-]$ corresponds to NaOH molarity
 Na_2O = (equivalent) percent Na_2O of the cement.
 w/c = water-cement ratio of the concrete

Using this equation, Figure 1 illustrates in graphic form relationships among the three variables. The NaOH molarity values plotted were calculated using the scatter in data on the high side (+0.06 moles/L in the equation) of the average. This provides somewhat conservative maximum cement alkali contents that would be required for safe levels of expansion.

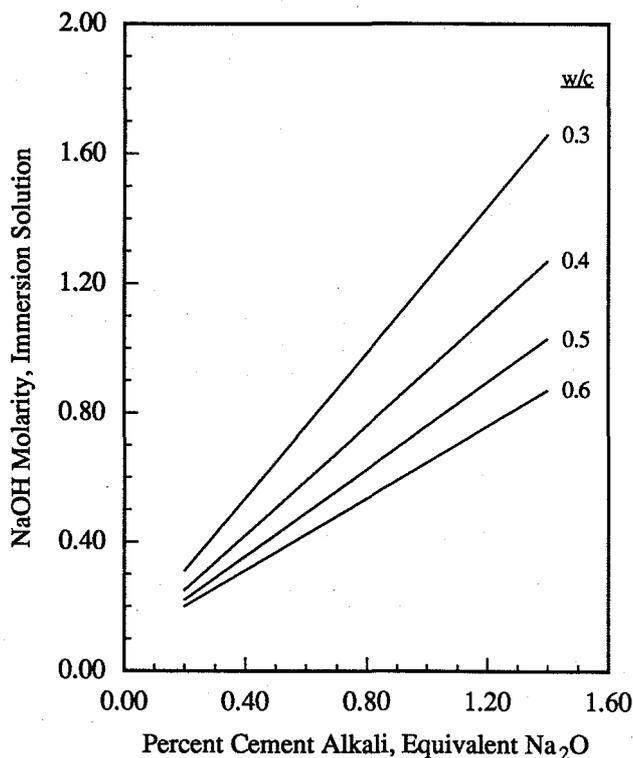


Figure 1 Relationship between cement alkali level and NaOH concentration of immersion solution for different w/c ratios

For example, for a w/c of 0.50, a 1.0 M NaOH solution corresponds to a cement alkali level of about 1.40%. This is the alkali concentration used in the NBRI and ASTM C 1260 test procedures. Since few cements, probably none in the United States, possess alkali levels of this magnitude, it is evident that the test solution is of greater alkalinity than is liable to be encountered in field concretes at 0.50 w/c. This in turn relates to the overly severe environment in the test procedure compared with the field and the tendency to find otherwise innocuous aggregates to be potentially deleteriously reactive. That is, field performance for the given aggregate is based on pore solutions of lower alkalinity because cement alkali levels do not reach 1.40% equivalent Na_2O . Thus, application of the test to determine more realistically the maximum safe cement alkali level can be approximated by adjusting the molarity of the immersion solution as indicated in the equation.

Another consideration, in field practice, is that the water-cement ratio may be of a lower value, such as 0.40, which is more characteristic of a structural concrete and corresponds to a cement alkali level of about 1.10%. However, a fixed water-cement ratio of 0.50 is essential in the immersion test because ASR depends upon diffusion of NaOH solution into the test specimens, and permeability of the mortar bar specimens under this test condition is strongly dependent upon water-cement ratio. Additionally, the question of cement content may be raised. The immersion test mortar bars are made at a fixed aggregate-cement ratio of 2.25:1.00, which is probably equivalent to a cement content in excess of 450 kg/m³ in concrete. At such high cement contents in concrete, the additional mitigating factors of increased strength and creep on ASR expansion potential should also be considered.

The evaluation of mineral admixtures using this immersion test also was first carried out by NBRI (Davies and Oberholster, 1987) and later by CSIRO (Shayan, 1990) and in the Strategic Highway Research Program (Stark, Morgan, Okamoto, and Diamond, 1993). In these investigations, it was concluded that the procedure would be useful in evaluating mineral admixtures, specifically fly ash and ground granulated blast furnace slag, for capability to prevent expansive ASR. Test results are presented in this paper to support this conclusion.

IDENTIFYING SAFE CEMENT ALKALI LEVELS

It is evident that, to identify maximum safe cement alkali levels, the 1.0 M NaOH solution concentration must be reduced to correspond to specific cement alkali levels at a given w/c. This need is due to the fact that the NaOH concentration is raised up to one molar to accelerate the reaction and to properly classify the slowly reacting aggregates. In determining a safe alkali level the test would be attempting to identify a specific cement alkali level for a specific aggregate regardless of relative susceptibility to the reaction. For example, it has been found that the 0.080% test criterion is the minimum expansion obtained with slowly reactive aggregates and the maximum obtained for innocuous aggregates at a 1.40% equivalent Na₂O of the cement (Stark, Morgan, Okamoto, and Diamond, 1993). Also, since field observations for the aggregates under study displayed evidence of expansive ASR at cement alkali levels less than 0.95% equivalent Na₂O, a failure criterion would have to be lower at 14 days for an immersion solution of 0.67M NaOH, which corresponds to 0.95% equivalent Na₂O of the cement, per the linear regression equation.

A number of aggregates were evaluated according to this approach, using four solution molarities to represent a range of cement alkali levels. All mortar bars were made using an ASTM Type I cement (8% C₃A) with 0.18% equivalent Na₂O, and a w/c of 0.50. Although alkali content of the mortar bar cement is generally believed to have little, if any, measurable effect on expansion, a very low alkali cement was used to further assure that virtually no alkali in addition to that provided by the immersion solution could bias the test results. Aside from the use of the 0.50 w/c and the adjusted immersion solutions, mortar bar casting and test storage were carried out in accordance with ASTM C 1260.

Aggregate composition, cement alkali level for deleterious ASR in field concrete, cement alkali level equivalent in the immersion solution, and 14-day expansion values for C 1260 testing conditions (1.0 M NaOH solution at 80° C) are given in Table 1. All results are averages for four companion mortar bars. These data reveal a progressive reduction in expansion with reduction in solution molarity (cement alkali equivalent), as would be expected. Even for aggregates not associated with ASR, expansion decreased with cement alkali equivalent but, in these cases, from an already innocuous expansion level. It should be noted that the cement alkali equivalents of the immersion solutions were calculated on the basis of the worst case for w/c of 0.50.

To determine the safe cement alkali level for an aggregate by this procedure, the expansion criterion must decrease with reduction in NaOH solution concentration as discussed previously. A plot of results from the present tests is given in Figure 2. The projected failure criterion (dashed line) is shown as being 0.08% at 1.0 M concentration. The criterion is subsequently shown to decrease at a rate dictated by the coincidence of the

Table 1 Results of tests to identify maximum safe cement alkali levels

Aggregate rock type	% cement alkali reported for deleterious ASR	Cement alkali equivalent, %, in immersion solution	14-day expansion, percent
Crushed gabbro	No ASR reported	1.40	0.026
		1.00	0.014
		0.75	0.011
		0.50	0.002
		0.24	0.002
Crushed dolomite	No ASR reported	1.40	0.023
		1.00	0.014
		0.75	0.011
		0.50	0.002
		0.25	0.006
Crushed granite gneiss	0.85 to 0.95	1.40	0.086
		1.00	0.042
		0.75	0.009
		0.50	0.004
		0.25	0.006
Mixed siliceous reactive chert and sandstone	0.95 to 1.05	1.40	0.272
		1.00	0.214
		0.75	0.040
		0.50	0.004
		0.24	0.005
Crushed metabasalt	0.80 to 0.90	1.40	0.096
		1.00	0.060
		0.75	0.032
		0.50	0.016
		0.25	0.010

curves for the gabbro, dolomite, and granite gneiss and the fact that the line falls below the field failure indicated for the granite gneiss. This convergence point should insure lack of ASR because both the gabbro and dolomite have known satisfactory service records. Therefore, data plotted for 1.40% cement alkali are results for 1.0 M NaOH concentration, as normally used. With reduction in NaOH concentration in the test, safe expansions are reduced to a maximum of 0.030 to 0.040% at 14 days. Any point below this line for an aggregate would represent a safe cement alkali level, while points above this criterion represent potential excessive expansion. Figure 2 indicates, for example, that any cement alkali level up to 1.40% is safe for the innocuous gabbro and dolomite aggregates. For the granite gneiss, which reacted deleteriously in the field at 0.85% to 0.95% alkali, the safe level would be about 0.70% alkali.

At the present time, further data are being developed to better define maximum safe cement alkali levels by this method before this approach can be used commercially.

IDENTIFYING MINERAL ADMIXTURES FOR PREVENTING EXPANSIVE ASR

As stated earlier, the rapid immersion test procedure appears to be adaptable to evaluating mineral admixtures for preventing expansion due to ASR. Studies were carried out in the present program to substantiate those findings.

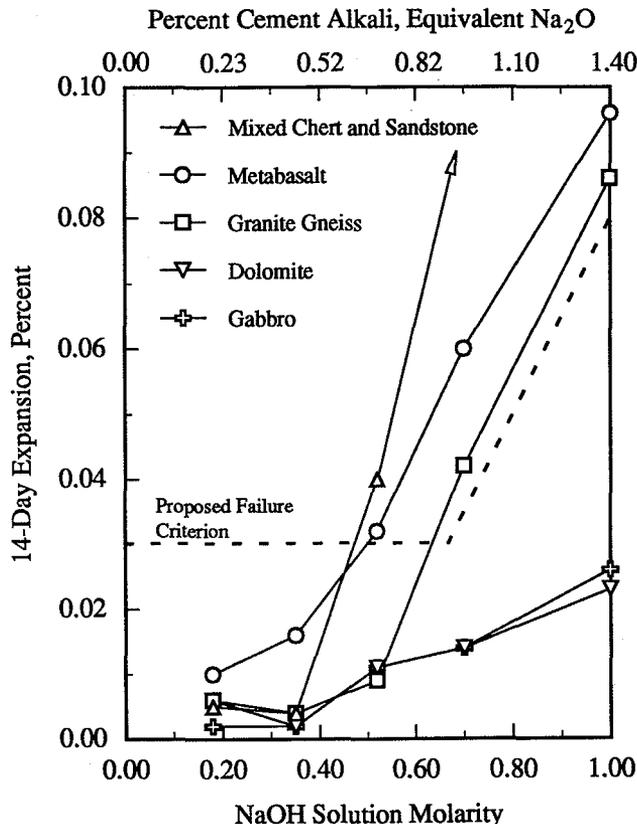


Figure 2 Projected failure criterion to determine safe cement alkali level for deleterious aggregates, using the rapid immersion test procedure with mortar bars at 0.50 water-cement ratio.

In one investigation, three fly ashes were evaluated in field pavement test sections and in the rapid immersion test as 20 to 25% mass replacements of an ASTM Type II portland cement with 0.50 to 0.60% equivalent Na₂O. One was an ASTM Class F fly ash with approximately 5% CaO. A second was a high-lime ASTM Class C fly ash with approximately 25% CaO, while a third was a 50:50 blend of the same high-lime fly ash and a second low-lime Class F fly ash from a different source. A highly reactive natural sand and gravel from a single source was used in both the pavement and rapid immersion tests.

Observation of the pavement after three years of service revealed the early development of longitudinal and map cracking characteristic of that due to ASR in pavements. The only test sections displaying such distress were those containing the high-lime Class C fly ash and the control sections with no fly ash. The sections containing the low-lime Class F fly ash or the fly ash blend were in excellent condition.

Results of the rapid immersion tests paralleled those noted in the test pavement. That is, control mixtures with no fly ash, and the mixture containing the high-lime Class C fly ash developed by far the greatest expansions. Mixtures containing the fly ash blend or the Class F fly ash developed little expansion, with the latter remaining below the test criterion of 0.08% at 14 days. These results thus indicate similar relative performance for the test pavement sections and the rapid immersion tests.

A second series of rapid immersion tests was run using known reactive aggregate from three sources together with two Class F fly ashes and one Class C fly ash. Characteristics of these fly ashes and the ASTM Type I portland cement used are given in Table 2.

Table 2 Composition of fly ashes and portland cement

<u>Analyte</u>	<u>Percent</u>			
	<u>Fly Ash No. 1</u>	<u>Fly Ash No. 2</u>	<u>Fly Ash No. 3</u>	<u>Portland Cement</u>
SiO ₂	51.40	48.71	33.00	21.22
Al ₂ O ₃	18.50	19.98	18.90	4.86
Fe ₂ O ₃	16.10	15.26	5.97	3.39
Total	86.00	83.95	57.87	—
CaO	4.49	5.67	27.00	65.25
MgO	1.06	1.31	5.28	0.52
S (sulfide)	1.43	0.67	2.60	2.38(SO ₃)
Total Na ₂ O	0.84	0.73	1.98	0.02
Total K ₂ O	2.34	2.53	0.39	0.25
Total Equivalent as Na ₂ O	2.38	2.39	2.25	0.18

The fly ashes were used in proportions up to 60% replacement of cement by mass. The quarried volcanics (metabasalt) aggregate with greatest expansion with no fly ash is from the same source as used in the test pavement. The source showing the least expansion without fly ash is a quarried granite gneiss, while the aggregate with an intermediate expansion is a chert-quartzite gravel. The cement used in this series contained 0.19% alkali as equivalent Na₂O.

Results in this test series are given in Table 3 where 14-day expansions are given for different cement replacement levels for the three fly ashes used with these aggregates. The data indicate that the two Class F fly ashes reduced expansions to below the failure criterion when used at the 20 to 30% cement replacement level, while the Class C fly ash failed to do so even when used at up to the 60% cement replacement level. Also, it is seen that the required proportion of fly ash to reduce expansions to below the test criterion varied somewhat with aggregate source.

Most importantly, the data show that reductions in expansion to below 0.10% were achieved only by the two ASTM Class F fly ashes. In an unpublished report, the writer obtained similar results in which Class F fly ashes at 20 to 30% levels of replacement for cement reduced expansions to below the test criterion, while Class C high-lime fly ashes could not achieve this level of reduced expansions.

The writer believes that differences in performance are related to lime-silica ratios of the calcium silicate hydration products of the cement and fly ash (Bhatty, 1985).

CONCLUSIONS

Results reported herein suggest that, with further refinement, the NBRI rapid immersion test can be used not only to determine whether an aggregate is potentially deleteriously reactive, but also to identify maximum safe cement alkali levels. Also, it appears that the procedure may be able to identify the capability of mineral admixtures to prevent excessive expansion due to ASR with respect to the proportion of fly ash required to do so with a particular aggregate and cement alkali level. Such use appears to require adjustments in either or both the failure criterion and the NaOH concentration of the immersion solution.

Table 3 Results of rapid immersion tests to evaluate fly ashes

Source, ASTM class	Fly ash Cement repl. level (%)	14-day expansion (%)		
		Reactive Aggregate Component		
		Volcanics	Granite gneiss	Chert, quartzite
None	0	0.867	0.309	0.409
No. 1, Class F	10	0.489	0.231	0.146
	20	0.054	0.064	0.000
	30	-0.001	0.008	-0.006
No. 2, Class F	10	0.623	0.247	0.232
	20	0.102	0.111	0.028
	30	—	0.040	0.014
No. 3, Class C	30	0.771	0.231	0.310
	45	0.510	0.178	0.230
	60	0.535	0.170	0.125

REFERENCES

- Bhatty, M.S.Y. 1985, 'Mechanism of pozzolanic reactions and control of alkali-aggregate expansion', *Cement, Concrete, and Aggregates*, 7(2), 69-77.
- Davies, G. and Oberholster, R.E. 1987, 'Use of the NBRI accelerated test to evaluate the effectiveness of mineral admixtures in preventing the alkali-silica reaction', *Cement and Concrete Research*, 17(1), 97-107.
- Helmuth, R. 1993, 'Alkali-silica reactivity: an overview of research', SHRP-C-342, Strategic Highway Research Program, National Research Council, Washington D.C., 13-16.
- Oberholster, R.E. and Davies, G. 1986, 'An accelerated method of testing the potential alkali reactivity of siliceous aggregates', *Cement and Concrete Research*, 16(2), 181-189.
- Shayan, A. 1990, 'Use of fly ash and blended slag cement in prevention of alkali-aggregate reaction in concrete', *Proc. Concrete for the Nineties Conference*, Leura, NSW, Australia, 17 pp.
- Stark, D., Morgan, B., Okamoto, P., and Diamond, S. 1993, 'Eliminating or Minimizing Alkali-Silica Reactivity', SHRP-C-343, Strategic Highway Research Program, National Research Council, Washington D.C., 48-63.