Prediction Aggregate Reaction Based on Chemistry and Nanostructure of Alkali-Silica Gels

Continuation Request to FHWA

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The alkali-silica reaction (ASR) is one of the most important mechanisms for deterioration of concrete, but there are significant difficulties with the current tests used to predict aggregate reactivity. We propose to continue our very successful current research on the mechanisms of ASR to develop new approaches to chemical-based tests for aggregate reactivity. This research is supported by FHWA using pooled state DOT funds. It is highly desirable to have a rapid and relatively easily implemented test of aggregate reactivity towards ASR, but, as described below, it is known that the standard chemical test (ASTM C 289, Standard Test Method for Potential Alkali-Silica Reactivity of Aggregates) does not always effectively indicate ASR behavior. The objective of the pooled fund study at UIUC is to understand reaction mechanisms so as to improve the predictive ability of this test. This document proposes three tasks to continue that study: 1) explore test modifications with measurements that more directly relate to the reaction chemistry, 2) modify certain details in the test procedure so it more accurately measures dissolved silica and reduction in alkalinity, and 3) improve interpretation of the existing test data by revising the boundary between reactive and nonreactive aggregates based on new understanding of the reaction process. These tasks range from major modifications in the test procedure to minor changes in the analysis of results.

The UIUC pooled fund study has provided important new understanding about the chemistry of the alkali-silica reaction on which test revisions can be based. Using X-ray diffraction and bulk chemical analysis, we have shown that the molecular structure of the alkali silicate hydrate gel can be modeled by the crystalline sodium silicate hydrate called kanemite[1]. The dominant Q^3 polymerization observed using ^{29}Si NMR spectroscopy and the presence of a basal X-ray diffraction peak show that sheet-like units dominate the local structure. Furthermore, the shift of the X-ray diffraction peak on wetting provides strong evidence that gel swelling is analogous to that of a clay mineral. The alkali silicate gels do not form when portlandite (calcium hydroxide) is available. As aggregate reacts, silica enters the pore solution and forms C-S-H by reaction with portlandite; this C-S-H is dominated by Q^1 polymerization. Only when portlandite has been used up do we observe formation of C-S-H dominated by Q^2 silicate polymerization and then alkali silicate hydrate gel dominated by Q^3 polymerization. In addition, our current work and a

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[1] Wieker et al., Materials Science of Concrete, 1998.

previously published study[2] using ^{29}Si NMR have identified significant concentrations of complex silicate species in the pore solution that are precursors to the formation of the ASR gel.

Taken together, these results constitute strong evidence that the alkali-silica reaction involves dissolution of the reactive aggregate, reaction of the dissolved silica with the hydrated cement paste and finally formation of the alkali silicate gel. Thus a chemical test such as C 289 that measures dissolution of aggregate therefore appears to be valid.

Results using C 289 do not always correlate with field experience. In some cases this discrepancy may be due to the limitations of this test. The test is designed to indicate whether an aggregate contains constituents with the potential to cause deleterious reaction in concrete. It does not incorporate issues known to affect concrete expansion such as the proportion of the reactive constituent, the effect of the aggregate microstructure (in particular the grain size and availability on surface of the reactive constituent), concrete history (temperature and moisture), and concrete restraint. However, the test is known to correlate poorly with other, longer duration tests (ASTM C 227 and C 1293) when applied to slowly reacting aggregates such as gneiss and to certain limestones, which exhibit a large reduction in alkalinity. As discussed above, our results indicate that a test based on aggregate dissolution is fundamentally valid, so it is the details of the test that need revision.

In the first task we will continue to explore basic issues in the reaction chemistry as the basis for a chemical test. The reaction of aggregate is controlled by dissolution and gel formation. Dent Glasser and Kataoka[3] showed that dissolution can be described using a silica-hydroxide solubility phase diagram in which the silica solubility (expressed as $[SiO_2]$) increases as hydroxide ($[OH^-]$ or pH) increases and different solid phases (e.g., quartz, cristobalite, opal, or glass) have different solubility curves that depend on their relative stability. The position of these solubility curves can be readily determined from a chemical test such as C 289, although the results are not normally evaluated in this way, and Dent Glasser and Kataoka discussed what controls of the $[SiO_2]$ – pH path in different situations. The diagram does not indicate the conditions required for formation of ASR gel and the relationship between these conditions and the solubility of the silica phase. We therefore propose to determine these conditions by systematically varying the solution composition and using NMR to identify gel products (as evidenced by Si with Q^3 polymerization). We recognize that the gel formation is not usually a thermodynamically controlled process and it may not be possible to characterize gel formation using phase equilibra, but if we can add a reasonably well constrained gel-forming region to the silica-pH solubility diagram, the C 289 results can be interpreted in a far more straightforward fashion.

In the second task, we will explore various modifications in the C 289 test procedure. Some of these modifications were proposed by Sorrentino et al.[4] in what they called a

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[2] Brough et al., J. Materials Science, 1996.

[3] Dent Glasser and Kataoka, Cement and Concrete Research, Vol. 11, pp. 1-9, 1981.

[4] Sorrentino, D., Clement, J.Y., Golberg, J. M., 9th International Conference on Alkali- Aggregate Reaction in Concrete, Westminster, London, Vol. 2, pp. 1009-1015, 1992.

kinetic test. ASTM C09.26 has balloted the kinetic test, but lacked sufficient comparative data on which to base acceptance. This task will directly examine these modifications and will provide such comparative data.

1. C 289 test uses phenolphthalein as the end point in the titration to determine [OH^-]. This end point was shown by Dent Glasser and Kataoka[5] to be invalid for this purpose. The kinetic test determines [Na^+] rather than [OH^-]. Measuring [Na^+] should also prevent the problems observed with certain limestones.
2. C 289 reduces aggregate to a particle size between 300 μm and 150 μm. Sorrentino et al.[3] showed that discarding particles smaller than 300 μm may alter the composition of the test specimen by preferentially removing reactive constituents. The kinetic test utilizes a particle size smaller than 150 μm to avoid altering the sample. The kinetics of dissolution clearly depend on particle size, and we will examine the use of smaller particle sizes in a more narrow size range to improve test precision.
3. In either C 289 or the kinetic test, gel precipitation would have the effect of reducing the apparent amount of reacted aggregate. People running C 289 have reported evidence of such precipitation. If we determine the conditions required for gel precipitation in Task 1 will allow us to modify the test parameters such that no gel precipitates.
4. Both C 289 and the kinetic test utilize NaOH as the test solution. We have studied the reaction in KOH; we find no difference in gel structure, but we find that the reaction is more rapid with K. For this reason, we will examine the use of KOH as the test solution.

As part of this task, we will also explore whether it is possible to follow the reaction by measuring swell as the aggregates react instead of [SiO_2] and [OH^-]. Such a procedure has been developed by Wen[6] and at the Texas Transportation Institute[7]. In engineering laboratories, it is much easier to measure swell than to determine chemical composition. In this procedure, however, it is important to control the test such that gel is produced and has access to water for swelling.

In the third task, we will reexamine the levels of [SiO_2] and reduction in alkalinity in C 289 that are associated with deleterious reaction in concrete. The current boundary curve was proposed by Mielenz and Witte[8] when it was not recognized that crystallographically strained quartz could cause deleterious reaction and the more aggressive ASTM C 1260 test required to detect reactive aggregates containing strained

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[5] Dent Glasser, L.S., and Kataoka, N., Cement and Concrete Research, Vol. 11, pp. 191-196, 1981.

[6] Wen, Z., and Yin, Q., Proceedings of the 5th International Symposium on the Cement and Concrete, pp. 1218-1225, 2002.

[7] Zollinger, D.G., and Sarkar, S.L., unpublished communication, 2003.

[8] Mielenz, R. C., and Witte, L. P., Proceedings, ASTM, Vol. 48, pp.1071-1103, 1948.

quartz had not been developed. We will reexamine this boundary curve using our own test data, data from participating DOTs, and any published data.

Results from any or all of these tasks should lead to improvements in the testing of alkali-reactive aggregates. By using these three different approaches, which vary from major to minor modifications in the current test procedure, we make a successful outcome much more likely.

The current pooled fund study at UIUC is a 3-year project that started July 2001, but funds were only provided for 2 years. This request is for $154K in additional funds to continue the project until July 2004.