

**INFLUENCE OF CEMENT PORE SOLUTION ON EXPANSION**

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ABSTRACT

The influence of the aqueous solution in the pores of hydrating mortar on alkali-silica reaction have been studied to improve our understanding of the reaction mechanisms. Mortar bar expansion studies were carried out using a variety of cements and aggregate materials. Pore solutions were expressed from nonreacting mortars at ages up to 28 weeks prepared using the same cements, and the solution compositions were determined. Responses of the same aggregate materials in model pore solutions (solutions similar in composition to the measured pore solutions) were studied. When results from these three experimental studies were synthesized, it was found that expansion correlated directly with the amount of silica dissolved in the model pore solutions at the same pH and the same reaction time. Therefore, at least for the materials studied, the dissolution of silica in model pore solutions appears to be a measure of the extent of alkali-silica reaction in mortars, and the resulting expansion (if water is freely available) appears to be a function of the extent of this reaction.

1. INTRODUCTION

Although there have been many descriptions of alkali-silica reaction in concrete since it was first reported, only general aspects of the mechanisms involved in the reaction and the resulting expansion are understood. Many details of the mechanisms are still being investigated and some are the subject of controversy. The goal of the study described here was to improve our understanding of certain details of the mechanisms. The study focussed on the influence of the composition of the aqueous solution in the pores of mortar. The work, carried out over a number of years, is fully described in the PhD thesis of the first-named author [1]. This presentation constitutes a summary of selected important features.

2. EXPERIMENTAL PROCEDURES

The experimental study consisted of three parts: 1) determination of mortar-bar expansions using a variety of cements and reactive aggregate materials, 2) determination of the compositions of pore solutions in

corresponding mortars not containing reactive aggregates, and 3) characterization of reactions of the aggregate materials with alkali hydroxide solutions (model pore solutions). The materials used were portland cement and sand-sized aggregate. Eight cements were used, selected to vary both the level of alkali and the types of alkali-containing phases. Three reactive aggregate materials were used: a moderately reactive opal, a slightly reactive quartzite, and a very slightly reactive gneissic granite. The nonreactive aggregate was limestone. Each reactive aggregate was used in combination with the limestone, and proportions of reactive aggregate were varied so as to bracket the pessimum level of each reactive material. Expansion tests were carried out according to ASTM C227-87, Standard Test Method for Potential Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method), except for the following: mortars were prepared using a single water-to-cement ratio of 0.485 (by mass), only a single batch (two bars) of each mixture was prepared, the bars were stored over water in sealed containers at room temperature (~22°C) instead of 37.8°C, and for most of the mortars, the expansion measurements were carried out for durations of 2 to 3 years.

Pore solutions were expressed from companion mortars prepared using the same cements and nonreactive limestone aggregate. The solutions were expressed from mortars at selected ages between 1 week and 28 weeks. These solutions were analyzed for their pH level and for concentrations of hydroxide, potassium, sodium, calcium, and silicate ions.

Model pore solutions solutions (mixtures of sodium and potassium hydroxide) were prepared at several hydroxide ion concentrations. Reactive aggregates, in the same sand-sized grading used for mortar-bar tests, were immersed using the same proportions of aggregate and solution as were present in the mortars. Progress of the reactions in these model solutions was followed by measuring pH levels and silica concentrations of solutions filtered at ages of 1, 2, and 3 weeks.

### 3. RESULTS

#### 3.1 Expansions

The mortar-bar expansion curves followed generally similar patterns for all cements and aggregates. Expansion began immediately, with no induction period apparent. The rate of expansion was highest at the beginning of the test for all types of reactive aggregate used. The rates decreased gradually and progressively, such that the rate after approximately 1 year was low and relatively constant for the duration of the test (in many cases in excess of 3 years).

The final expansions were greatest for mortars containing opal and high-alkali cements; they produced expansions from 0.1 percent to 0.4 percent. The final expansions were much lower, below 0.06 percent, for mortars containing opal and low-alkali cement, and for mortars containing quartzite or granite and high-alkali cement.

Among mortars containing a particular reactive aggregate, there were significant differences with respect to both the initial rate and final level of expansion produced by each cement. In mortars containing opal, the four high-alkali cements produced substantially greater levels and initial rates of expansion than the four low-alkali cements. However, differences

in the final expansion levels could not be explained solely in terms of differences in the alkali levels among the eight cements.

### 3.2 Pore Solution Compositions in Nonreactive Mortars

The compositions of pore solutions expressed from companion mortars without reactive aggregate provided an indication of the solution composition generated for each cement. This defines the environment in which reaction would occur if reactive material were present. Analyses of the pore solutions expressed from nonreactive mortars hydrated for periods between 1 week and 28 weeks showed that the levels of most constituents varied with age in a smooth, regular fashion.

The pH levels ranged from 13.4 to 14.0, and the hydroxide ion concentrations ranged from 322 mM to 965 mM. All four low-alkali cements produced ultimate pH levels below 13.6, while each of the four high-alkali cements produced levels above 13.6.

The sodium ion concentrations found in these pore solutions ranged from 6 mM to 279 mM. As expected, the potassium ion concentrations were higher, from 75 mM to 857 mM. The calcium ion concentrations were much lower, ranging from 0.6 mM to 2.2 mM. The measured concentrations of dissolved silica were even lower, all less than 0.05 mM.

Individual concentrations of sodium and potassium in solution varied with from cement to cement, as the contents of individual alkalies in each cement varied. However, it was found that measured pH and hydroxide ion levels were proportional to the total alkali content of the cement.

### 3.3 pH and Dissolved Silica in Model Pore Solutions

Each aggregate material was allowed to react in a series of model pore solutions, and the resulting levels of pH and dissolved silica were measured. These measurements were made to determine whether differences in expansion produced by different cement-aggregate combinations could be related to differences in the rate of dissolution of the reactive siliceous component in pore solutions produced by the different cements. Therefore, the ratio of aggregate to solution was selected to duplicate the proportions of reactive material in the mortars for expansion tests, and the model pore solutions approximated the alkali concentrations and pH levels of the pore solutions expressed from nonreacting mortars containing limestone.

On visual inspection after filtering, all solutions appeared clear and free of precipitated silica or visible gel. Nevertheless, and to our surprise, the opal produced extremely high concentrations of dissolved silica and large reductions in pH. Silica concentrations produced by opal ranged from 100 mM to 2400 mM. At the same time, reductions in pH in excess of 1 pH unit were recorded. In contrast, the quartzite produced only moderate levels of dissolved silica, typically around 10 mM, and no measurable reduction in pH. The granite produced lower levels of dissolved silica, typically around 1 mM, and no measurable reduction in pH.

Silica levels measured in pore solutions expressed from actual mortars containing opal are usually only a few millimoles per liter [2]. The levels of dissolved silica found in the model pore solutions were approximately

three orders of magnitude higher than those expected in actual mortar pore solutions. Much greater reductions in alkali concentration were also found in these model solutions than in actual mortars. The reductions expected for opal-bearing mortars are approximately 100 mM [3]; the reductions found in the model solutions were 700 mM. The much higher levels of dissolved silica and the great reduction in hydroxide ion concentration in the model pore solutions are thought to be a consequence of the fact that the model solutions contained no calcium.

The aggregate reactions in the model systems were studied for only 3 weeks. However, the levels of dissolved silica and pH changed considerably between 2 weeks and 3 weeks, indicating that the aggregate dissolution processes had not terminated. Therefore, any interpretations can only be tentative.

#### 4. DISCUSSION

It was found that the level of dissolved silica varied with the proportion of reactive aggregate in the same pattern shown by the variation in mortar-bar expansion with the proportion of reactive aggregate. Therefore, we set out to explore a possible relationship between the levels of dissolved silica in model pore solutions and expansion levels of the corresponding mortars.

Levels were estimated of dissolved silica expected in actual mortars if no calcium were present. This estimation was based as follows on the concentrations of dissolved silica found in the model solutions. The silica concentration levels produced by the reactive materials increased with increasing initial pH of the model solution. This relationship was well defined for opal, less so for quartzite, and uncertain for granite, which produced so little dissolved silica. This relationship was used to estimate the level of dissolved silica expected at each age (1, 2, or 3 weeks) from each aggregate proportion, based on the measured pH levels in the expressed pore solutions.

Expansions of the actual mortar bars at the same ages (1, 2, or 3 weeks) were then compared with the estimated silica concentrations, as shown in Figure 1. While there is significant scatter, there is also a clear correlation between expansion of the actual mortar bars and the estimated level of dissolved silica.

There are fundamental differences between aggregate reactions in mortar and in the model pore solutions used in the present study. Besides the differences in silica concentration and reduction in pH discussed previously, gel due to the reaction is observed in mortars, whereas there was no visible evidence of gel in the model solutions. These differences indicate that the solutions used in the present study modelled only the aggregate dissolution process.

We infer that formation of gel requires that calcium be present. However, mortar-bar expansion, which depends primarily on gel formation and swelling, was found to correlate with levels of silica produced in model pore solutions, which reflect only aggregate dissolution rates. This correlation included expansions measured at all three ages for which levels of dissolved silica were determined in the model solutions. The correlation

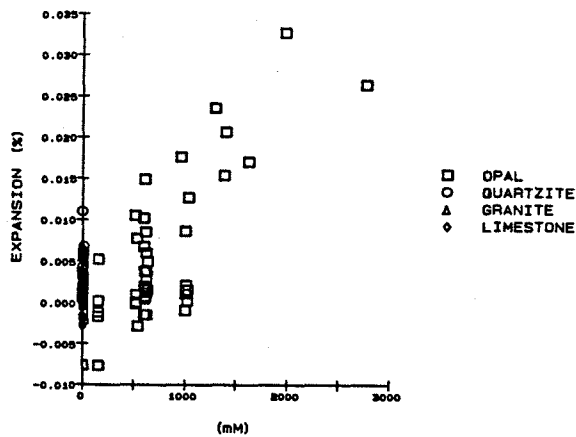


Figure 1. Measured mortar-bar expansion levels versus estimated reaction parameter based on silica concentration during reactions of each aggregate material in model pore solutions.

suggests that the rates of aggregate dissolution and gel formation for a given system may similar to each other, i.e., that dissolution may be the rate controlling process in the overall alkali-silica reaction.

## 5. CONCLUSIONS

The expected concentration of dissolved silica if no gel were to be formed was estimated for a variety of mortars, prepared with various cements and various reactive aggregates in various proportions. The parameter was based on the concentrations of silica produced in model alkali-hydroxide pore solutions, which in turn depended on the initial pH of each solution. Measured expansion produced by each mortar (each aggregate, at each proportion, with each cement) was found to correlate with this estimated reaction parameter. This result suggests that alkali-silica reaction involves at least two steps, dissolution of silica from the aggregate, and subsequent precipitation of a silica-bearing reaction product. It appears that dissolution of silica in model pore solutions may provide a measure of the extent of this reaction in mortars, and that expansion (if water is freely available) may be a function of the extent of this reaction. The extent of reaction in the model solutions is shown to depend on the specific aggregate material, its proportion relative to the amount of solution, and the pH level of the solution.

## 6. ACKNOWLEDGEMENTS

These studies were carried out both at Martin Marietta Laboratories and at the National Institute of Standards and Technology, and were supported in part by National Science Foundation Grant No. CEE 82-10791.

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