Alkali-Silica Reaction in a Form of Chemical Shrinkage

Kai-Wei Liu1,*, Anol Kanti Mukhopadhyay2

1Zachry Department of Civil Engineering, Texas A&M University, College Station, 77843, Texas, United States
2Texas A&M Transportation Institute, Texas A&M University, College Station, 77843, Texas, United States
*Corresponding Author: kaiwei@tamu.edu

Abstract The current approach of ASR testing and mitigating damaging ASR heavily depends on accelerated mortar-bar tests (AMBT) and concrete prism tests (CPT). Although these approaches have resulted significant advances in avoidance of ASR damage in concrete, it was found to have limitations and drawbacks. Therefore, there is a growing demand for an ASR test method to overcome the above issues. A chemical approach that simulates aggregate-pore solution reaction that exists in concrete has been proposed in this study while as-received aggregates were immersed in alkaline solution (i.e., 1N NaOH + CH) and allowed to react at a relatively high temperature (i.e., 80°C). The approach measures solution volume change in a form of chemical shrinkage over time as the reaction between aggregates and solution proceed. The tested aggregates were categorized based on the measured chemical shrinkage. The aggregates that are failed by AMBT but passed by CPT and vice versa were identified by this method, and an ASR mechanism in terms of chemical shrinkage was proposed. The results indicate that the proposed test measures solution volume contraction due to ASR and has the potential to predict aggregate alkali reactivity in a short period of time.

Keywords Alkali-Silica Reaction, Chemical Shrinkage, Solution Volume Contraction, ASR Mechanism

1. Introduction

Alkali-silica reaction (ASR) in Portland cement concrete is a deleterious chemical reaction which induces expansive stress in presence of sufficient moisture. Since the ASR-related problems were identified in the early 1940s, extensive research has been carried out on ASR over the decades. The development of ASR test methods to assess ASR potential of aggregates and concrete through a simulative type of approach was one of the main focus areas of that research. The main purpose of an ASR test method is to measure aggregate reactivity prior to their use in concrete structures. The most commonly used ASR testing heavily depends on the accelerated mortar bar test (AMBT) and concrete prism test (CPT). The aggregates tested for AMBT (e.g., ASTM C 1260[1]) require crushing and the test results are unrelated to field performance. Marks[2] used AMBT to evaluate ASR reactivity of 30 sands and concluded that more research was needed due to mismatch of AMBT and field performance. Swamy[3] stated that AMBT is problematic due to aggregate crushing and higher amount of cement than those used in concrete construction. The results obtained from AMBT cannot be applied to concrete. Mukhopadhyay et al.[4] stated that when aggregates are tested according to AMBT, a good ASR field performance can sometimes be classified as reactive due to aggregate crushing. Aggregates are heterogeneous materials containing a random distribution of reactive constituents (e.g., reactive siliceous impurity in limestone or reactive cementing materials in sandstone). Either losing or exposing the reactive phases during aggregate crushing will result aggregates being passed/rejected by AMBT but rejected/passing by field performance. The CPT (e.g., ASTM C 1293[5]) has been considered as the best index for field performance[6-9] but the test duration imposes a major drawback [4,10]. Therefore, there is a growing demand for an ASR test method to overcome some of the above limitations.

A chemical approach has been developed using a device named volumetric expansion measurement device (VEMD) which simulates the aggregate-pore solution reaction that exists in concrete to overcome some of the limitations in the current ASR test methods. As-received aggregates (without crushing) were immersed in alkaline solution (i.e., 1N NaOH (NH) + Ca(OH)2 (CH)) at a relatively high temperature (i.e., 80°C) and measures free volume change due to ASR over time. The measured ASR volume change over time is in a form of chemical shrinkage. This chemical approach is applied to measure the alkali-silica reactivity of aggregates in terms of solution volume contraction in a short period of time.

2. Objectives

The main objectives are to provide a chemical test method
that can measure aggregate reactivity in a short period of time and to understand the ASR mechanism in this method. The primary tasks that are conducted to fulfill the above objectives are (i) testing borosilicate glass balls with 1N NH + CH alkalinity at 80°C and measuring its chemical shrinkage as a proof of concept, (ii) testing different aggregates (both fine and coarse without crushing) and measuring their reactivity in terms of chemical shrinkage, (iii) proposing an ASR mechanism in terms of chemical shrinkage, (iv) testing the aggregates that are failed by AMBT but passed by CPT and vice versa, and (v) comparing the chemical shrinkage, 14-day AMBT, and 1-year CPT expansion values for the tested aggregates and establishing the degree of matches and miss-matches in terms of reactivity between these three test methods. As a result, the proposed test method can (i) provide an ASR mechanism in terms of chemical shrinkage which might occur in concrete as well, and (ii) serve as an alternative to the current ASR methods before the aggregate is used for concrete design and thereby, to avoid concrete durability issues due to ASR.

3. Materials and Methods

3.1. Materials

Pure phase material (i.e., borosilicate glass balls) and aggregates (both fine and coarse) (Table 1) were tested in this study. Table 2 presents the design of experiments, i.e., the effective factors and their levels. Twelve aggregates with different types of reactive silica characterized by petrographic observation (i.e., ASTM C 289[11]) and varying ranges of reactivity (i.e., AMBT, CPT) were selected (Table 1). For each aggregate, an average of two replicas with distilled water and three replicas with 1N NH + CH at 80°C were conducted.

3.2. Methods

The device (Fig. 1) consists of a container, a teflon-coated brass lid, a hollow tower, and a steel float. The container and tower are made of stainless steel whereas the lid is made of naval brass. At the top of the tower, a casing is installed to ensure proper alignment of the linear variable differential transducer (LVDT) and the float.

Table 1. List of Aggregates with Relevant Material Data

| Aggregate | Type | AMBT (14-day Expansion, %) | CPT (1-year Expansion, %) | Reactive Constitute (ASTM C 289) |
|-----------|------|-----------------------------|--------------------------|----------------------------------|
| FA1       | Fine | 0.554                        | -                        | Acid volcanic, Chert, high strained QTZ |
| FA2       | Fine | 0.334                        | 0.171                    | High strained QTZ, Chalcedony, Chert |
| FA3       | Fine | 0.317                        | 0.058                    | Low strained QTZ, Chalcedony, Chert |
| FA4       | Fine | 0.242                        | 0.043                    | High strained QTZ, Chert          |
| FA5       | Fine | 0.079                        | 0.035                    | Few siliceous (e.g., Chert) inclusions |
| CA1       | Coarse | 0.417                      | 0.078                    | Acid volcanic, Chert              |
| CA2       | Coarse | 0.250                      | 0.047                    | High strained QTZ, Chert          |
| CA3       | Coarse | 0.227                      | 0.071                    | Chalcedony, Chert                 |
| CA4       | Coarse | 0.179                      | 0.149                    | Chalcedony, Chert                 |
| CA5       | Coarse | 0.140                      | 0.020                    | Limestone, limited separate Chert  |
| CA6       | Coarse | 0.040                      | 0.129                    | Chalcedony, Chert                 |
| CA7       | Coarse | 0.012                      | 0.027                    | Few siliceous (e.g., Chert) inclusions |

FA: fine aggregate; CA: coarse aggregate; QTZ: quartz
The LVDT used has a maximum range of 2 inches with a sensitivity of 0.84 mV/V/0.001 inch. The LVDT is placed with an O-ring located at the bottom of the casing and secured with six set screws through the side of the casing. A thermocouple with compressing fitting is inserted through the side of the container to measure the temperature of the soak solution. The devices are filled up with as-received aggregate (approximately 8-9 lbs) and alkaline solution of 1N NH + CH and tested at 80°C inside an oven according to the experimental design in Table 2. The 1N NH solutions are prepared by diluting 40g of sodium hydroxide crystals into 0.9 liter of distilled water. Water is added to raise the total volume of solution to 1 liter. Calcium hydroxide crystals are then added (1g per liter solution) to the above respective NH solution slightly above saturation in order to prepare an alkaline solution saturated with calcium hydroxide. Adding calcium hydroxide crystals slightly above the saturation point ensures presence of undissolved CH crystals, which represents a situation similar to concrete pore solution. Thorough mixing ensures homogeneity of all the prepared solutions. The weight of the oven-dried material corresponded to the 80 percent volume of the container. A constant aggregate/solution volume ratio and gradation for all the aggregate were tested in Table 2.

### Table 2. Factors and Levels in the Design of Experiments

| Factors            | No. of Levels | Level Description                                                                 |
|--------------------|---------------|-----------------------------------------------------------------------------------|
| Material type      | 1             | pure phase+ 12 aggregates                                                          |
|                    | 2             | Borosilicate glass+ 12 aggregates in Table 1                                      |
| Temperature        | 1             | 80°C                                                                               |
| Solution Type      | 2             | Distilled Water+ 1N NH with CH                                                     |

The test procedure is summarized below:

- Keep the device filled up with clean and dried aggregate and alkaline solution overnight at room temperature to allow maximum saturation of voids in the alkaline solution.
- Place the device on a vibrating table and conduct vacuuming under vibration for 2 hours to mainly remove entrapped air bubbles in the solution. This also helps to saturate the unfilled voids (likely to be present) in aggregates after overnight saturation.
- Place the device inside an oven and heat it to 80°C (~6 hours).
- Apply a second stage vacuuming under vibration of 45 minutes to facilitate further removal of air bubbles (may be generated during heating at 80°C) from solution.
- The device was placed inside an oven, whose temperature was then raised to 80°C. It takes around 5–6 hours to reach the target temperature.
- Solution volume changes as the chemical reaction between aggregate and alkaline solution progresses; this makes the float move. As the float moves inside the tower, the stainless steel rod attached with the float also moves inside the LVDT. Through the data acquisition system, the computer records LVDT readings over time.

LVDT reading at the stable target temperature represents the reference (initial) LVDT reading for calculating displacement due to ASR. This ensures separation of thermal expansion from ASR. All LVDT readings after temperature stabilization minus the reference LVDT reading represent displacement due to ASR over time. The percent volume change of solution due to ASR is calculated by using (1).

\[
V(\%) = \frac{\Delta V_{\text{ASR}}}{V_{\text{Aggregate}}} \times 100
\]

Where:
- \( V(\%) \) = Percent volume change of solution due to ASR
- \( \Delta V_{\text{ASR}} \) = Solution volume change due to ASR
- \( V_{\text{Aggregate}} \) = Initial volume of aggregate

### 4. Result and Discussion

#### 4.1. Calibration

To check smooth float movement and ensure that the devices are leak-proof, water testing at 80°C with the same testing duration for all the devices were conducted. Each device was filled up with water, vacuumed with vibration (to remove air bubbles), and then placed inside the oven where it experienced a temperature change from the starting temperature (50-55°C) to 80°C. The water in the container experiences thermal expansion due to the temperature increase, which makes the float move upward. The float displacements (in inches) and solution temperatures data for all the devices were recorded over four days and are presented in Fig. 2. The figure shows that when the temperature reaches 80°C, the float also reaches a stable displacement level in all the devices. The float movement doesn’t change thereafter. This verifies that the devices are leak-proof and no measurable evaporation loss situation during the 4-day test duration.
Alkali-Silica Reaction in a Form of Chemical Shrinkage

4.2. Pure Phase Material

The use of borosilicate glass as a highly alkali silica reactive material has been reported both in conducting ASR research and ASR test developments [12,13]. The composition of the borosilicate glass balls is composed of SiO$_2$: 81 percent, Na$_2$O: 4 percent, Al$_2$O$_3$: 2 percent, B$_2$O$_3$: 13 percent. This is a zero-porous (i.e., absorption capacity–0% material). The tests run with distilled water and 1N NH + CH alkalinity at 80°C were conducted. Fig. 3 shows the net solution volume changes in a form of contraction over time at 80°C from borosilicate glass balls–solution (water and 1N NH + CH) test. Fig. 4 shows the present of reaction product due to ASR on a borosilicate glass ball surface. The presence of mainly Si with some amount of Na was evident from energy-dispersive spectroscopy (EDS) analysis. These observations suggest that ASR occurs in the device, and the device measures net solution volume contraction due to ASR between the borosilicate glass balls and alkaline solution. Note that glass balls are non-porous and there was no effect due to absorption (similar to aggregate absorption phenomena, i.e., pore spaces of aggregates filled with water/solution) on the measured net solution volume change. Therefore, based on the borosilicate experiments, it can be postulated that this approach in closed-system measures solution volume contraction due to ASR over time.

Figure 2. (a) Temperatures and (b) Float Displacements (Small Oscillations are due to LVDT Sensitivity) over Time in all the Devices from Water Tests

Figure 3. Net Solution Volume Change from Borosilicate Glass Balls with Water and 1N NH + CH Solution at 80°C

Figure 4. Secondary Electron Images of Reaction Products on a Borosilicate Glass Ball with Different Magnification: (a) Original, Na/Si: ~0.25, (b)(c)(d) 1N NH + CH at 96 hours, Na/Si: 1.46 to 2.59

Bates et al.[14] found that borosilicate glass alters differently from neutral to alkaline solutions. The formation of surface layers on glass is caused by constituent elements of the glass passing into solution, with the elements initially in solution diffusing into or being adsorbed onto the glass. This surface layer (usually called ASR gel) consists of:

- An innermost diffusion layer (partially hydrated and depleted of soluble elements (i.e., B and Na).
- An outermost precipitated layer (amorphous and crystalline phases). 
A gel layer (amorphous and crystalline phases) between them.

The structure and/or composition of the surface layer differ from the original glass and are formed by more than one reaction process (i.e., ion exchange, water diffusion, network hydrolysis and condensation, and precipitation) occurring simultaneously. Therefore, the measured volume change in a form of chemical shrinkage in this study represents a combined effect of all the above processes. These processes are similar to the different steps of the reaction mechanisms of ASR. The measured net solution volume change in this study is a manifestation of the combined effects of different steps in the reaction mechanisms. Therefore, it is logical to say that the chemical shrinkage of borosilicate glass measured represents a combined effect of multi-steps ASR reaction mechanisms with dissolution–precipitation possibly the dominating factor.

4.3. Aggregates

For each aggregate, three replicas were conducted. Eight devices were simultaneously run inside an oven for four days. All aggregates were tested according to the experimental design in Table 2 and net solution volume change over time was measured. Fig. 5 shows the average measured volume change over time with 1N NH\textsubscript{+}CH of alkalinity at 80°C for all materials. Fig. 6 presents repetition data for all the aggregates. Note that net solution volume contraction over time was also invariably measured for all the tested aggregates (irrespective of coarse or fine aggregates). This is in agreement with earlier findings [4].

![Figure 5](image1.png)  
**Figure 5.** Average Solution Volume Change with 1N NH\textsubscript{+}CH at 80oC for All Materials

![Figure 6](image2.png)  
**Figure 6.** Repetition of Solution Volume Change with 1N NH\textsubscript{+}CH at 80oC for (a) Fine, (b)(c) Coarse Aggregates

Aggregate absorption capacity is affected by its porosity/permeability which can be divided into two categories: porosity and crack porosity. The change of crack porosity is associated with the aggregate thermal decompaction and mineral composition. The crack porosity...
increases with an increase of temperature due to different thermal expansion of the minerals in aggregates [15]. However, during the preheat step of the sample preparation procedure (section 3.2), the effect of crack porosity is eliminated. For the porosity, it has been reported that the permeability of tight rocks decreases with an increase in temperature from 20 to 200°C, and the relative change of porosity has no change with an increase of temperature [16]. Amro and Benzagouta [17] also found that the permeability of carbonate reservoir rocks reduced significantly when temperature raised from 25 to 50°C and the reduction is in a continuous trend up to 100°C. Therefore, the effect of aggregate absorption/permeability in measuring net solution volume change in this test would be very negligible.

Concrete aggregates that have high absorption capacity reach 85 percent of their total absorption capacity in less than 30 minutes of soaking in water, and reach 95 percent of their AC within 24 hours of soaking in water [18]. The total submerged time of aggregate in alkaline solution before achieving the stable target temperature in the test is around 26±1 hours. Moreover, the two-stage vacuum saturation is a part of the sample preparation procedure (section 3.2), which enhances absorption (should be more than 95 percent). It is extremely difficult to fully saturate (i.e., achieving 100 percent absorption capacity) an aggregate by prolonging soaking time. Therefore, it is unlikely that the saturation (pore filling by solution) will continue during testing (i.e., four days). Even if this continues, it would be very negligible. The dominant phenomenon is net solution volume contraction due to ASR.

Measuring chemical shrinkage in fine aggregate-alkaline solution system over time has been reported earlier by Kundsen [19]. In Kundsen’s procedure, sand samples were boiled for 3 hours to eliminate the effect of absorption capacity. A flask is filled up with sand samples and 10N NaOH solution, and then stored in a thermostatic bath at 50°C. The researchers used the data solution volume change over time (recorded manually) to calculate chemical shrinkage due to ASR over time. The chemical shrinkage was used as a measure of aggregate reactivity. The authors stated that the measured chemical shrinkage in their test procedure is very similar to the cement hydration. The total volume (cement and water) decrease and the volume of calcium silicate hydrate (C-S-H) increase during cement hydration. Similarly, when ASR occurs in concrete, water coming from outside the system allows the ASR gel to expand and to occupy a volume greater than the amount of water in the reaction. This test was widely used in Denmark.

In earlier work [4], the subtraction of net water volume change over time (water curve) in aggregate-water test from the net solution volume change over time (solution curve) in aggregate-solution test was adopted as an indirect way to measure solid volume change due to ASR. A net upward displacement was observed based on four coarse aggregates testing and interpreted as a measure of solid volume increase, i.e., expansion. In this study, aggregate-water tests at 80°C were conducted for all the aggregates in Table 3.1. Deductions of water curves from solution curves are performed and the net displacements after water curve deduction are summarized in Table 3.

Table 3. Net Displacement after Water Deduction for All Aggregates

| Net displacement | CA  | FA  | All Aggregates |
|------------------|-----|-----|----------------|
| Occurrence, %     | U   | D   | U   | D   | U   | D   |
| 86               |     |     |     |     | 100 |     |
| 14               |     |     |     | 50  |     | 50  |

Table 3 shows that the consistent trend of upward movement after deducting the water curves from solution curves is not obtained. The coarse aggregates shows higher percentage of net upward displacements (sometimes with very less upward movement) than the fine aggregates. Based on these findings (inconsistent trends), it is concluded that simply deducting water curves from solution curves does not necessarily provide direct measurement of solid volume change (i.e., expansion). The water curve can be considered a perfect reference curve if the aggregate-water system remains totally inert (i.e., no reaction between tested aggregates and water at high tested temperatures). However, the following discussion indicates that this assumption may not be correct.

Researchers found that the solubility of amorphous silica depends on both temperature and pH value. Morey et al. [20] and Alexander et al. [21] observed that the solubility of amorphous silica in water increases with an increase of temperature shown in Fig. 7(a). Alexander et al. [21] also concluded that the solubility was about 0.012% to 0.014% in the pH range 5 to 8 at 25°C and increased at high pH (pH > 8) (shown in Fig. 7(b)) because of the formation of silicate ion in addition to Si(OH)4 in solution. This phenomenon is also observed from borosilicate glass tested with distilled water in this study (Fig. 3).

Figure 7. Solubility of Amorphous Silica in (a) Water and (b) Different pH Solution at 25oC [21]

It has been found that solubility of limestone depends on inclusion, temperature and pH value. The solubility of limestone in water increases with an increase in calcite and decreases with an increase in dolomite in limestone [22]. Paler [23] also showed that the solubility of calcite decreased with an increase of temperature when the limestone was in
alkaline solution. Regardless of the temperature change, the solubility of calcite increases with a raise of pH in solution. Therefore, it is unlikely that aggregate-water system remains inert at high temperatures and water curves obtained from aggregate-water tests do not serve as a good reference curves. This explains the inconsistency of the results in Table 3.

4.4. ASR Mechanism in terms of Chemical Shrinkage

ASR is the reaction between the hydroxyl (OH-) ions present in pore solution and reactive siliceous component(s) in aggregates. The alkali cations (i.e., Na+, K+, Ca²⁺, etc.) are important because their presence in high concentration leads to an equally high concentration of hydroxyl to maintain equilibrium in the pore solution. When they are incorporated into the ASR gel, the role of alkali becomes relevant. In general, there are four steps in the chemical reaction mechanism of ASR [24-27]. Although the reaction mechanisms that govern ASR are well understood, the mechanism in terms of chemical shrinkage due to ASR has not been clearly explained. Based on the results in this study, a mechanism between aggregate and solution due to ASR in a closed system is proposed. A decrease of net solution volume is due to the combined effects of: (i) Si-O-Si bond breaking and silica dissolution which cause solution volume decrease, (ii) consumption of reactants such as water and ionic species which causes solution volume decrease, (iii) ASR product formation and expansion which cause solution volume increase, (iv) solution going into micropores (pores that developed due to the formation of high-volume less dense ASR products) and microcracks related to the degree of ASR which cause solution volume decrease, and (v) incomplete absorption (negligible but may be responsible for slight solution volume decrease) in a closed system condition of the device.

4.5. ASR Reactivity in terms of Chemical Shrinkage

The net solution volume changes over time for all the tested materials with 1N NH₄OH + CH at 80°C are presented in Fig. 5. Any curve of aggregate in Fig. 5 represents an average of three replicas (i.e., repetition of the same test run three times shown in Fig. 6). The solution volume change at 96 hours for all the tested aggregates along with AMBT 14-day expansion (%) and CPT 1-year expansion (%) are listed in Table 4 and graphically presented in Fig. 8.

In Fig. 6, some displacement curves show slightly dropped and/or flat movements are due to combine effects summarized below:

- Aggregate alkali-silica reactivity is a function of the form/degree of crystallinity, grain size, texture, and nature of distribution/proportion of the reactive silica within the aggregate. When ASR products form along the grain boundaries of reactive silica within aggregates, the swelling stress is built after the products absorb water. Cracks form when the swelling stress exceeds the tensile strength of the aggregate. Further cracks occurs because ASR does not stop at this point as those cracks create fresh surfaces and act as open passages for alkali solution to flow into the matrix of the aggregate leading more solution level reductions. Therefore, the slightly dropped movements in Fig. 6 might be caused by new open passages due to new cracks formations.

- None or slowly reactive aggregates (e.g., FA3, FA5, CA5, and CA7) are not considered susceptible to ASR due to few disordered structure of silica phase in aggregates. It requires longer time for ASR to occur and thus leads to very little solution level change. When the solution level change is under the LVDT sensitivity, flat movements will be recorded in the displacement curves in Fig. 6.

| Table 4. Measured Net Solution Volume Contraction along with AMBT and CPT |
|-----------------------------|-------------------------------|---------------------|---------------------|
| Material              | Net Solution Volume Contraction | CPT 1YR Exp.% | AMBT 14D Exp. % |
|------------------------|--------------------------------|----------------|------------------|
| Borosilicate Glass, 0.25" | 0.200                          | -               | -                |
| FA1                    | 0.156                          | -               | 0.554            |
| FA2                    | 0.105                          | 0.171           | 0.334            |
| FA3                    | 0.033                          | 0.058           | 0.317            |
| FA4                    | 0.081                          | 0.043           | 0.242            |
| FA5                    | 0.026                          | 0.035           | 0.079            |
| CA1                    | 0.106                          | 0.078           | 0.417            |
| CA2                    | 0.145                          | 0.047           | 0.250            |
| CA3                    | 0.038                          | 0.071           | 0.227            |
| CA4                    | 0.062                          | 0.149           | 0.179            |
| CA5*                   | 0.029                          | 0.020           | 0.140            |
| CA6**                  | 0.119                          | 0.129           | 0.040            |
| CA7                    | 0.014                          | 0.027           | 0.012            |

*: Failed by AMBT but Passed by CPT; **: Passed by AMBT but Failed by CPT
An average of three replicas was conducted in Fig. 5 in order to overcome the above mentioned issues. Since the same batch materials tested in each device might have different siliceous inclusions within aggregates, the dropped and flat movements can be eliminated through an average of repetitions.

For highly reactive aggregates (e.g., FA1 and CA1) the presence of in-situ type reaction products were observed (Figs. 9 and 10). For a slowly reactive aggregate, the presence of surface etching and cracking was observed with no obvious presence of gel within 4 days of the testing period. Note that $Q_3$ to $Q_1$ transformation (a swelling process [28]) can be responsible for aggregate volume expansion without forming any typical ASR gel. Therefore, it may be possible to measure some volume change due to ASR with no obvious presence of ASR products in case of slowly reactive aggregates. From the above discussion, it is logical to claim that microstructural studies on the reacted aggregate particles by SEM-EDS support the reactivity prediction in this study.

Here are some observations on Table 4 and Fig. 8:
- The more the volume contraction, the higher the reactivity becomes. In general, a high 14-day expansion of AMBT and 1-year expansion of CPT match with higher volume contraction values. This indicates that the proposed test procedure can measure ASR aggregate reactivity within a short period of time (i.e., four days). Volume change in a form of chemical shrinkage can serve as a measure of ASR aggregate reactivity.
- A representative volume contraction can be determined by testing aggregate with a test solution of 1N NH + CH alkalinity at 80°C.
- Consistently identified the aggregate (e.g., CA5 and CA6) that the AMBT method has passed/failed, but which the CPT has failed/passed in a short period of time.
- The ASR aggregate criteria are proposed based on the number of aggregates that are tested in this study. The criteria of volume contraction of 0.03% are applied to distinguish ASR reactivity between non-reactive and reactive aggregate. However, the ranges are arbitrary in nature at this time. To establish an effective ASR aggregate classification system, assignment of more refined volume contraction ranges through testing greater number of aggregates is highly warranted.
5. Conclusions

The proposed chemical test measures solution volume contraction due to ASR over time and has the potential to predict aggregate alkali reactivity in a short period of time. The following conclusions based on the results and discussions in this study can be drawn:

1) The experiments with pure borosilicate glass balls support measuring net solution volume contraction over time and used to validate the proposed approach.
2) A decrease of net solution volume is due to the combined effects of:
   - Si-O-Si bond breaking and dissolution (solution volume decreases).
   - Consumption of reactants such as water and ionic species (solution volume decreases)
   - Product formation and expansion (solution volume increases)
   - Solution goes into micropores (pores that developed due to the formation of high-volume less dense ASR products) and microcracks. The degree of micropore and microcrack formation is related to the degree of ASR (solution volume decreases)
   - Incomplete absorption (negligible but may be responsible for slight solution volume decrease) in a closed system condition in the device
3) Deduction of water curves from solution curves does not provide an effective way to directly measure solid volume change (i.e., expansion). Therefore, the requirement of conducting parallel aggregate-water tests is not needed and facilitates reduction of total testing time.
4) The proposed chemical approach has the potential to overcome the limitations of the current test methods (e.g., AMBT) and has the ability to identify the aggregates that belong to false positive and negative categories (i.e., passed by AMBT but failed by CPT and vice versa) in a short period of time.
5) The proposed test measures aggregate alkali silica reactivity in a short period of time in terms of measuring volume contraction. The formation of ASR product is observed by SEM-EDS on the reacted aggregate surfaces for the pure phase borosilicate glass and reactive aggregates (Figs. 4, 9, and 10). It is evident that microstructural studies on the reacted aggregate particles by SEM-EDS support the volume contraction based reactivity prediction.
6) The results in Fig. 8 show that the aggregate that is failed by AMBT but passed by CPT (i.e., CA5) has a relatively low solution volume contraction (slowly reactive or almost non-reactive). On the other hand, the aggregates that are passed by AMBT but failed by CPT (i.e., CA6) have a relatively high solution volume contraction (reactive). Therefore, the proposed chemical test method (i.e., 1N NH + CH at 80°C) has the potential to identify the aggregates that are passed/failed by AMBT but failed/passed by CPT in a short period of time. This is one of the benefits of this method. However, the test conditions (e.g., 1N NH + CH at 80°C) may be server and unrelated to the field levels of alkalinity. An attempt has been made to develop an effective kinetic energy-based ASR approach to represent the kinetic type of ASR combined effects of alkalinity, temperature, and moisture.

REFERENCES

[1] ASTM C 1260-07. Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), American Society for Testing Materials, West Conshohocken, Annual Book of ASTM Standards, Vol.04.02, 677-681, 2008.

[2] V. J. Marks. Characteristics of Iowa Fine Aggregate, Report, MLR-92-6, Iowa Department of Transportation, 57, 1996.

[3] R.N. Swamy. Testing for Alkali-Silica Reaction, The Alkali Silica Reaction in Concrete, Blackie and Sons, Glasgow, 54-95, 1992.

[4] A. Mukhopadhyay, H. Ghanem, C. S. Shon, D. Zollinger, D. Gress, D. Hooton. Mitigation of ASR in Concrete-Combined Materials Test Procedure, Innovative Pavement Research Foundation Report, IPRF-01-G-002-03-2, 2009.

[5] ASTM C 1293-08a. Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction, American Society for Testing Materials, West Conshohocken, Annual Book of ASTM Standards, Vol.04.02, 682-688, 2008.

[6] D. S. Lane. Comparison of Results from C 441 and C 1293 with Implications for Establishing Criteria for ASR-Resistant Concrete, Cement, Concrete, and Aggregates, Vol.21, No.2, 149-56, 1999.

[7] M. D. A. Thomas, F. A. Innis. Effect of Slag on Expansion Due to Alkali-Aggregate Reaction in Concrete, ACI Materials Journal, 95, 716–724, 1998.

[8] M. D. A. Thomas, F. A. Innis. Use of the Accelerated Mortar Bar Test for Evaluating the Efficacy of Mineral Admixtures, Cement, Concrete, and Aggregates, Vol.21, No.2, 157-164, 1999.

[9] B. Fournier, V. M. Malhorta. Evaluation of Laboratory Test Methods for Alkali-Silica Reactivity, Cement, Concrete, and Aggregates, Vol.21, No.2, 173-184, 1999.

[10] S. Bauer, B. Cornel, D. Figurski, T. Ley, J. Miralles, K. Folliard. Alkali-Silica Reaction and Delayed Ettringite Formation in Concrete: A Literature Review, Report, 0-4085-1, Center for Transportation Research, Texas Department of Transportation, 2006.

[11] ASTM C 289-07. Standard Test Method for Potential Alkali Reactivity of Aggregate (Chemical Method), American Society for Testing Materials, West Conshohocken, Annual Book of ASTM Standards, Vol.04.02, 179-185, 2008.

[12] C. P. Ostertag, C. Yi, P. Monteiro. Effect of Confinement on
Alkali-Silica Reaction in a Form of Chemical Shrinkage

Properties and Characteristics of Alkali-Silica reaction Gel, ACI Materials Journal, Vol.104, No.3, 276–282, 2007.

[13] ASTM C441-05. Standard Test Method for Effectiveness of Mineral Admixture or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali-Silica Reaction, American Society for Testing Materials, West Conshohocken, Annual Book of ASTM Standards, Vol.04.02, 250-252, 2008.

[14] J. K. Bates, C. R. Bradley, E. C. Buck, J. C. Cummame, W. L. Ebert, X. Feng, J. J. Mazer, D. J. Wronkiewicz. High-level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics, U.S. Department of Energy, Vol. 2, 1994.

[15] V. Zharikov, E. B. Lebedev, A. M. Dorfman, V. M. Vitovtova. Effect of Saturating Fluid Composition on the Rock Microstructure, Porosity, Permeability and Vp under High Pressure and Temperature, Physics and Chemistry of the Earth, Vol.25, No. 2, 215-218, 2000.

[16] Y. Deng. Permeability and Porosity of Tight Rock Materials under Conditions of High Temperature and High Pressure, Applied Mechanics and Materials, Vols.170-173, 719-722, 2012.

[17] M. M. Amro, M. S. Benzagouta. Effect of pressure and temperature on petrophysical characteristics in the case of carbonate reservoirs, Oil Gas European magazine, Vol.35, No.2, 74-78, 2009.

[18] M. P. Adams, B. Gray, J. H. Ideker, J. E. Tanner, A. Jones, B. Fournier. Applicability of Standard Alkali-Silica Reactivity Testing Methods for Recycled Concrete Aggregate, Proceedings of the 14th International Conference on Alkali Aggregate Reaction in Concrete, Austin, Texas, 021811-ADAM, 2012.

[19] T. Knudsen. A Continuous, Quick Chemical Method for the Characterization of the Alkali-Silica Reactivity of Aggregates, Proceedings of the 7th International Conference on Concrete Alkali-Aggregate Reactions, Ottawa, 289-293, 1986.

[20] G. W. Morey, R. O. Fournier, J. J. Rowe. The Solubility of Amorphous Silica at 25oC, Journal of Geophysical Research, Vol.69, No.10, 1995-2002, 1964.

[21] G. B. Alexander, W. M. Heston, R. K. Iler. The Solubility of Amorphous Silica in Water, Journal of Physical Chemistry, Vol.58, No.6, 453-455, 1954.

[22] A. Hazim, A. Kawaz. Dissolution Rate Constant of Carbonates under Natural Environments, Tikrit Journal of Pure Science, Vol.15, No.3, 2010.

[23] A. N. Palmer. Origin and Morphology of Limestone Caves, Geological Society of America Bulletin, Vol.103, No.1, 1-21, 1991.

[24] L. S. D. Glasser, N. Kataoka. The Chemistry of Alkali-Aggregate Reaction, Cement and Concrete Research, Vol.11, No.1, 1-9, 1981.

[25] H. Wang, J. E. Gillott. Mechanisms of Alkali-Silica Reaction and Significance of Calcium Hydroxide. Cement and Concrete Research, Vol.21, 647–654, 1991.

[26] A. B. Poole. Alkali-Silica Reactivity Mechanisms of Gel Formation and Expansion, Proceedings of the 9th International Conference on Alkali-Aggregate Reaction in Concrete, London, England, 782–789, 1992.

[27] E. Garcia-Diaz, D. Bulteel, Y. Monnin, P. Degrugilliers, P. Fasseu. ASR Pessimum Behaviour of Siliceous Limestone Aggregates, Cement and Concrete Research, Vol.40, No.4, 546-549, 2010.

[28] E. Garcia-Diaz, J. Riche, D. Bulteel, C. Vernet. Mechanism of Damage for the Alkali Silica Reaction, Cement and Concrete Research, Vol.36, 395–400, 2006.