An **IPRF** Research Report

Innovative Pavement Research Foundation

Airport Concrete Pavement Technology Program

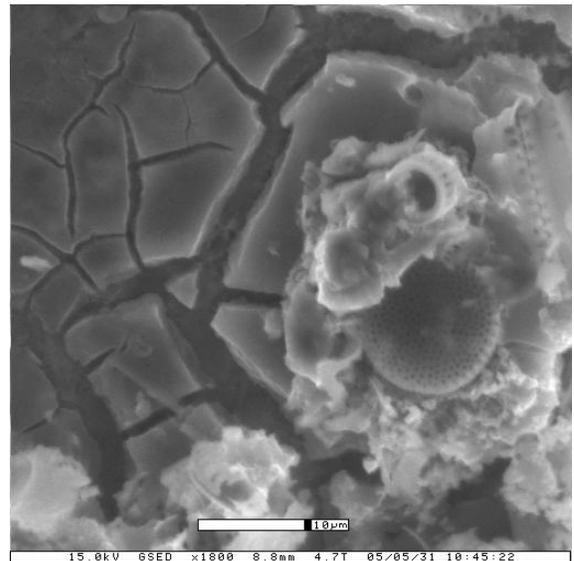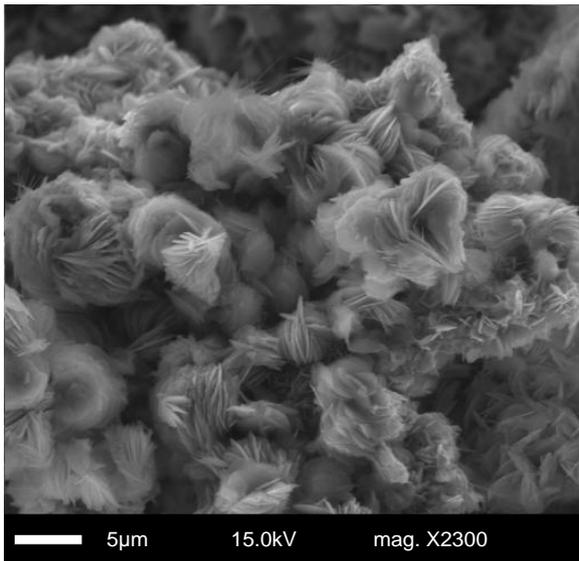**Report IPRF-01-G-002-02-5.1**

Evaluation of Alkali Silica Reactivity of Mineral and Aggregate Using Dilatometer Method

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5420 Old Orchard Road
Skokie, IL 60077   **June 2005**

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Evaluation of Alkali Silica Reactivity of Mineral and Aggregate Using Dilatometer Method

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EXECUTIVE SUMMARY

Measurement of volume change due to ASR of pure minerals and aggregates using the dilatometer device is a new approach. Dilatometer was used to measure ASR volume expansion in mineral / aggregate – solution system as a function of temperature, alkalinity and time. The volume expansion – time trend was modeled in order to derive rate constants at multiple temperatures. Activation energy was then calculated based on rate constant and temperature (1/T) relationship.

The test results showed that the energy needed to start ASR is comparatively low in case of mineral with high reactivity (e.g., Opal). In other words, the mineral with high reactivity needs less energy to initiate the reaction. Degree of crystallinity of different forms of silica minerals matches with the activation energy results, i.e., the lower the energy the lower is the crystallinity (e.g., amorphous or cryptocrystalline nature) and higher is the reactivity. The activation energy appears to vary with the reactivity where it is greater for the aggregate than that of the mineral.

The results indicate that the concept of activation energy can be used to represent the reactivity of mineral and aggregate subjected to ASR. The activation energy appears to be useful approach to categorize different form of silica minerals based on their reactivity. Dilatometer test is capable to determine the ASR potential of mineral / aggregate in terms of activation energy within a short period of time (e.g., 2-3 days) and is based on the direct measurement of expansion of ASR gel produced.

BACKGROUND

Alkali-silica reaction (ASR) in concrete is a deleterious chemical reaction that can produce expansive stresses. It generates polygonal cracking of aggregate and cracks in the paste that can eventually compromise the integrity of the concrete. The mechanism of ASR has been described as the reaction of certain types of aggregates containing reactive forms of silica with alkalis such as potassium, sodium, and calcium hydroxide mainly from cement hydration to form a gel around the reacting aggregate particles. When this gel is exposed to moisture, it expands, creating forces that cause tension cracks to form around the aggregate. Unconfined concrete undergoing ASR exhibits telltale signs of surface map cracking. Once cracking has initiated, more moisture penetrates the concrete, thus accelerating ASR.

The basic approach to mitigation of ASR is to control the factors that affect it, such as material combinations, alkalinity, aggregate reactivity, humidity, and temperature (Figure 1). ASR results from combination of all these factors. Once a concrete has been placed, its potential and extent for undergoing ASR will depend on external factors such as the conditions it is exposed to.
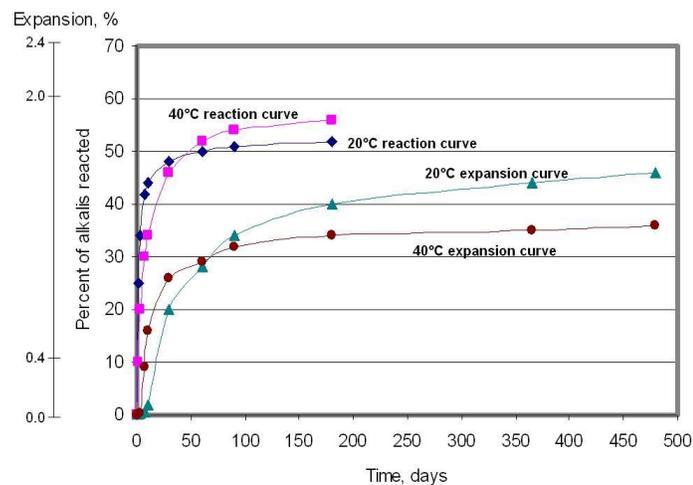
Figure 1 Effect of temperature and alkalinity on ASR expansion (Diamond et.al., 1981)

Figure 1 shows the effect of temperature and alkalinity on ASR expansion. Since expansion increases with increasing temperature and alkalinity, it is important to understand how material properties and exposure condition can be manipulated to control ASR expansion to tolerable levels.

Especially, the fine and coarse aggregates, which normally constitute about 75 percent of the volume of concrete, have a considerable effect on properties of concrete. The size, crystallinity, texture, and nature of the aggregate constituents not only govern the degree of

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physical compatibility of the components, but also affect the durability of concrete (e.g., ASR in concrete) subject to changes in environment. Therefore, proper characterization of aggregate properties will enable us to predict the behavior of concrete with high precision, which in turn lead to better control of ASR.

Recently developed at Texas Transportation Institute, a testing apparatus called a dilatometer has been used to carry out tests for determining alkali-silica reactivity of minerals and aggregates (both coarse and fine aggregates). This procedure can be done within a fairly short period of time (~ 4 days), and is based on the direct measurement of expansion of ASR gel produced. Expansion is measured on both mineral and aggregate. The test is accelerated by testing at elevated temperature of 60°C, 70°C, and 80°C. Although the test apparatus measures the expansion directly, it does not provide absolute values of expansion, but characteristics of it. In other words, the expansion data can be used to define parameters related to the formation of ASR gel.

OBJECTIVE

This research focuses on the use of dilatometer to measure alkali silica reactivity of common reactive siliceous minerals of varying crystallinity and some selective aggregates. ASR activation energy was introduced as a characteristic reactivity parameter to represent alkali silica reactivity of minerals and aggregates.

A series of ASR free volume expansion measurements as a function of temperature and alkalinity were performed using the dilatometer for both minerals and aggregates. The trend of volume expansion over time was modeled in order to derive rate constants at different temperatures. Activation energy was calculated based rate constant and temperature relationship.

TESTING PROTOCOL APPROACH

ASR is a chemical reaction that integrates the combined effects of temperature, alkalinity, moisture and time relative to the kinetics of ASR expansion. Increasing the temperature at early age increases the rate of chemical reaction that occurs between the alkalis and reactive silica in the aggregate and as a result higher expansions takes place during the early life of the concrete, but lower at later age (Figure 1). Ludwig (1981) studied the effect of humidity and temperature on mortar bars cured for 3 years and found the critical humidity required to prevent ASR damage is less than 85 percent. Aggregate alkali silica reactivity is a function of form/degree of crystallinity, grain size, and the proportion of the reactive silica within the reactive aggregate (Stanton 1940; Mindess, 2003) as well as alkalinity and temperature. Hobbs (1988) reported the expansion increases as particle size decreases, which means the particle size of reactive material is also an important factor. Diamond (1983) and Kolleck et al. (1986) suggests that a threshold concentration required to initiate and sustain ASR is 0.25M (pH=13.4) and 0.2M (pH=13.3), respectively. Below the threshold concentration (i.e., low pH solution), a reactive aggregate may not react (or

have low potential to react) and can show good field performance. It is clear from the above discussion that ASR is a kinetic type chemical reaction. Therefore, kinetic type model can be used to derive characteristic material properties and assess ASR fundamentally. In the past, researchers have investigated the use of a kinetic type ASR model for either the prediction of mortar bar expansion (T. Uomoto, Y. Furusawa, and H. A. Ohga, 1992) or for better interpretation of the existing test methods (Johnston et al. 2000).

Approach for Determining Alkali Silica Reactivity of Aggregate

The fundamental understandings of ASR mechanisms along with the above discussion suggest a simple chemical test method for the evaluation of mineral / aggregate reactivity. Aggregate alkali silica reactivity can be determined chemically by simulating aggregate - pore solution reaction that may exist in concrete. The test device should be capable to measure free volume change due to ASR over time. As-received aggregate can be tested in alkaline solutions of varying concentration (similar to and higher/lower than concrete pore solution concentrations) and at different temperatures within a short period of time. By selecting relatively higher testing temperatures (e.g., 60, 70 and 80°C) the reaction can be accelerated as ASR is dominantly thermally activated reaction. A simple chemical test of this nature will be rapid in nature and allow for the determination of the fundamental ASR material properties of aggregate unimpeded by an external diffusion process. The approach for determination of aggregate alkali silica reactivity is described stepwise below:

1. Measure volume change over time as a function of temperature, and alkalinity using dilatometer – the dilatometer procedure measures volume expansion produced by the alkali-silica gel when an aggregate / mineral reacts with alkaline solution. The test is conducted using three different normalities of NaOH solution, namely 1N, 0.5N and 0.25N. This helps to establish the reactivity of the aggregates as a function of the alkalinity to which the concrete is likely to be exposed to under field conditions.
2. Formulation of performance-based model–characterizes the measured time-expansion trend and derives characteristic reactivity parameters (e.g. rate of expansion, ultimate expansion, activation energy). From the foregoing discussion, it is clear that some initial conditions related to alkalinity, aggregate reactivity, moisture, and temperature conditions that must be met to initiate ASR. Activation energy can serve as a single chemical material parameter to represent this kinetic type combined effect of temperature, alkalinity, and time to evaluate ASR susceptibility of aggregate.

Development of a Kinetic-type Performance Model to Assess ASR

As previously noted, ASR is a chemical reaction that integrates the combined effects of temperature, alkalinity, and time relative to the kinetics of ASR expansion. The ultimate

expansion of aggregates, the theoretical initial time of ASR expansion, the rate constant are all important parameters in connection with ASR kinetics. To better account of the non-linearity, these parameters are encompassed within a kinetic-type performance model (equation 1) that is the proposed primary tool to characterize ASR (Figure 2) expansion behavior.

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0}.e^{(\frac{\rho}{t-t_0})^{\beta}}$$

(1)

where :

$\varepsilon_0 = $ ASR ultimate expansion

$\beta = $ Rate constant

$t_0 = $ Initial time of ASR expansion (hr)

$\rho = $ Time corresponding to an expansion (ε_0 / e)

By fitting the model (equation 1) to measured expansion data over time, the above four parameters (i.e., ε_0, β, t_0, ρ) are back calculated.
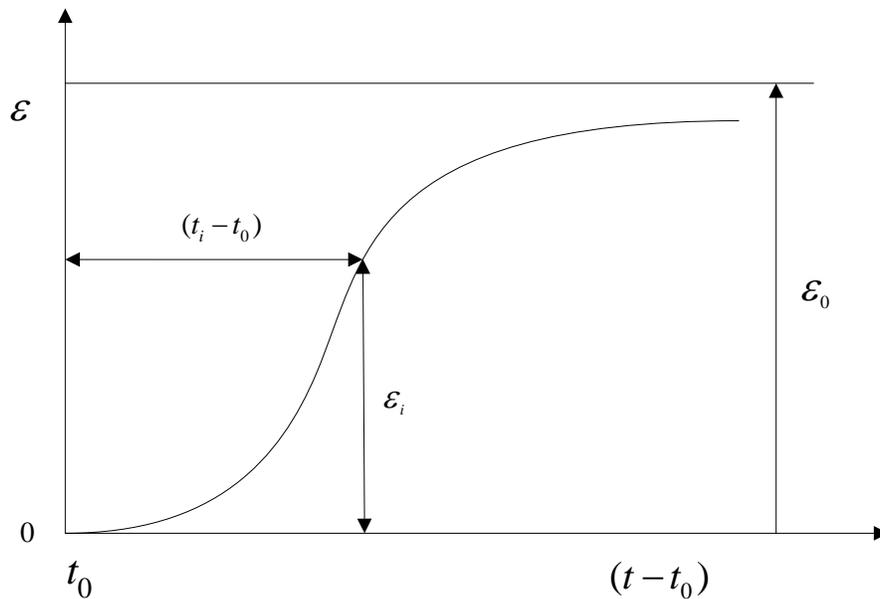

Figure 2 Proposed ASR Model to fit the expansion data history of the dilatometer.

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Determination of ASR Activation Energy

Equation (1) can be transformed into a linear form to facilitate the evaluation of the β parameter (which is. equivalent to the rate constant) by taking the double natural logarithm.

$$Ln\left[-Ln\left(\frac{\varepsilon}{\varepsilon_0}\right)\right] = \beta Ln\alpha - \beta Ln(t - t_0) \qquad (2)$$

Figure 3 display the ideal linear relationship between $Ln\left[-Ln\left(\varepsilon/\varepsilon_0\right)\right]$ and $Ln(t - t_0)$.

The β is calculated from the slope of the regression line (as in Figure 3). The β values at multiple temperatures (minimum 3 temperatures) are then determined and activation energy is calculated by plotting ln(β) versus (1/T) (as in Figure 4). Based on rate theory (Callister 2002), the slope of the linear regression (Figure 4) is equal to (-E_a/R) where R is the universal gas constant and E_a is the activation energy.

In analytical chemistry, activation energy (E_a) is defined as the minimum energy required for a chemical reaction to proceed (Ebbing et al. 2005). Consequently, it can be considered as an energy barrier. For ASR, E_a is considered as the minimum energy required initiating ASR taking into account the combined effect of alkalinity, temperature and time. It is important here to mention that the ASR E_a should be considered as a compound activation energy as aggregate is a heterogeneous material that is often composed of different mineral phases, i.e., reactive phases (one or more phases) and non-reactive phases (crystalline minerals).
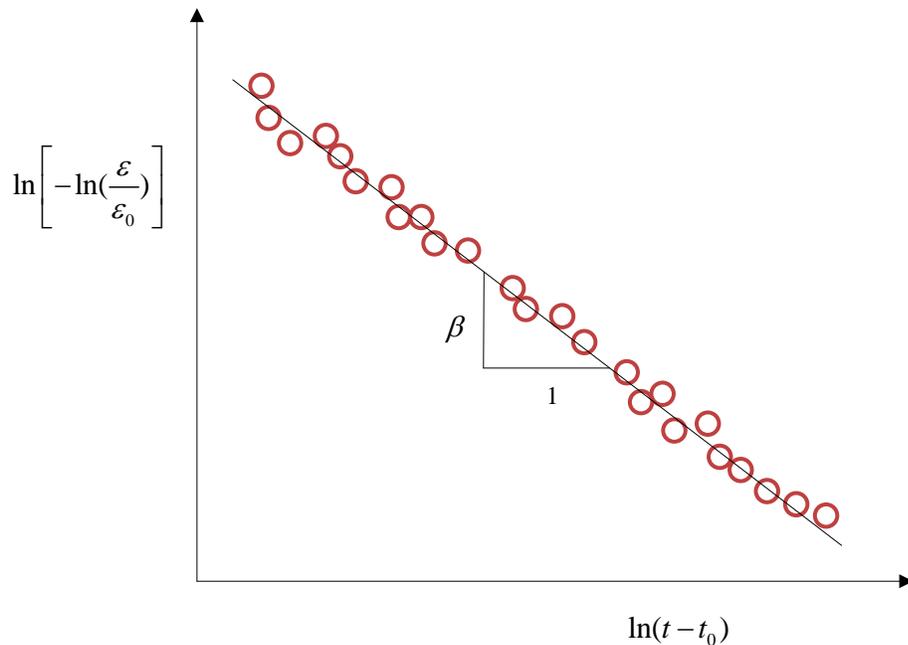

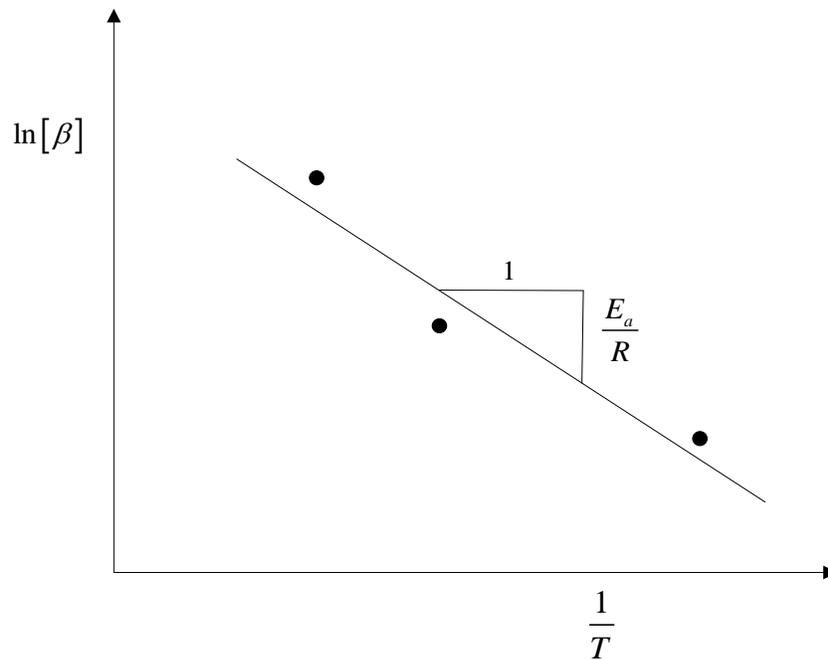Figure 3 Linearization of the kinetic performance model.

Figure 4 Determination of activation energy.

EXPERIMENTAL PROGRAM

The material selection, sample preparation, test device, test procedure, and data analysis are briefly described below:

Materials

Samples of different forms of reactive silica minerals, namely pure opal, chalcedony, jasper, splint along with a siliceous reactive (strained quartz) fine aggregate, and a reactive coarse aggregate (New Mexico rhyolite) were used for this study. Following is a brief description of each form of silica mineral.

Opal - Hydrous form of silica (SiO_2, nH_2O). Water content commonly 4-9% but can range up to more than 20%. Opal may be entirely amorphous to X-rays or may contain submicroscopic cristoballite with a disordered structure and excess water. Opal may occur as constituent of cherts, flints, volcanic rocks, some shales, sandstones etc. Its detection in concrete aggregates is important as amounts as small as 1% can cause damaging expansion due to ASR.

Chalcedony - Crypto- to microcrystalline variety of silica. In optical microscope, chalcedony is seen to be composed of radiating fibers of quartz. Electron microscopy

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observation has shown chalcedony consist of minute quartz crystals. Chalcedony has a submicroscopic spongy (porous) structure, with pores sometimes filled with water (similar to opal) and air. Chalcedony present as the main constituent of flints, cherts, jaspers, and as a cementing agent in quartzites. Chalcedony is considered to be a reactive mineral with cement alkalis, but researcher has shown that other disordered forms of quartz are the reactive species in flints and cherts.

Flint - Siliceous rocks composed of microcrystalline or cryptocrystalline silica.

Jasper - A dense, opaque, microcrystalline variety of quartz, usually red, brown or yellow and colored by oxides of iron.

Siliceous reactive sand - It contains strained quartz, i.e., quartz with crystal defects imposed through deformation. Strained quartz is highly reactive in alkaline solution.

New Mexico Rhyolite - An amorphous natural acid glass produced by the rapid cooling of molten lava. Volcanic glasses may be devitrified, thus forming groundmass of submicroscopic crystals. Acid glass tends to be more reactive than basaltic glasses, since they are more nearly completely siliceous.

Research team has selected the above mentioned forms of silica based on the available information on their reactivity and degree of crystallinity. Opal is a highly reactive form of amorphous silica. Knowledge of opal reactivity will help to understand the reactivity of well known Spratt limestone. Chalcedony and jasper belongs to cryptocrystalline silica group with intermediate reactivity. Flint is a rock mainly composed of chalcedony/submicroscopic quartz. By testing chalcedony, jasper and flint, research team will get a chance to throw some light on prediction of aggregate activation energy based on mineral activation energy.

Sample preparation

Minerals, which are produced from warehouse sources, had different particle size distribution (PSD). In general, the reactivity increases as the size of mineral or aggregate decreases. The amount retained on each sieve was kept constant for all the tested minerals to make the gradation as consistent as possible. This allowed for the comparison of the activation energy of different forms of silica minerals and to categorize them based on their reactivity. Figure 5 shows particles size distribution of minerals and aggregates used in this study. The New Mexico rhyolite shows relatively finer PSD than that of the tested minerals. The aggregate sample size is approximately 80 percent by volume of the dilatometer pot. The solution level was maintained at a fixed level as a standard for the solid/solution volume ratio.
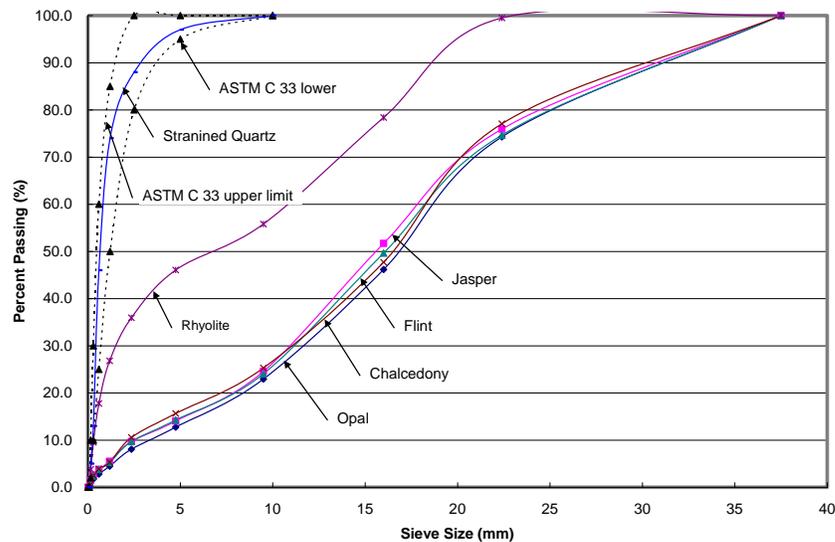
Figure 5 Particle size distribution of the tested minerals and aggregate.

Test device

Recently developed at the Texas Transportation Institute, Texas A&M University, a testing apparatus called a dilatometer (Shon et.al., 2002; Sarkar et al., 2004) has been used to determine the percentage volume change due to ASR over time for minerals and as-received aggregates in mineral/aggregate-solution reaction.   The cross sectional diagram of the dilatometer is shown in Figure 6. The dilatometer consists of a pot, a teflon-coated brass lid, a hollow tower, and a float. The pot and tower are made of stainless steel whereas the lid is made of naval brass. An LVDT is attached to the float, which is connected to a computer. After the container is filled with the material to be tested for ASR related expansion, the lid is closed and the device is immersed in a water bath. The temperature of the water bath is raised to the desired temperature. As ASR commences inside the dilatometer, expansive ASR gel is produced. The stainless steel rod attached with the float moves inside the LVDT, which generates electrical signals and continuously recorded digitally in the computer. The test period is relatively short (within 3 days) and can account for the direct measurement of expansive ASR product produced.

Dilatometer Testing Procedure

The procedure for dilatometer testing is summarized in Table 1 and briefly described below:

    a. The weight of the oven dried aggregate to fill 80 percent of the pot volume is measured and then placed in the dilatometer.

    b. The aggregate is soaked for 12-14 hours into the selected alkaline solution at room temperature (23°C).

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c. The lid and the tower is placed on the pot with the plastic float (attached to the threaded steel and LVDT rod) pre-placed inside the tower. The tower is screwed to the lid.
d. The dilatometer is subjected to 2-3 hours of vacuuming and vibration at room temperature to remove air bubbles from solution. The entrapped air during aggregate immersion in alkaline solution (step "b") and air that released due to aggregate absorption stay in the solution as air bubbles. To facilitate removal of air bubbles, the inner surface of the lid is designed at a specific slope.
e. The dilatometer is then placed in a water bath to raise the temperature to the selected target temperature.
f. The dilatometer is removed from the water bath and subjected to a second round of vacuuming and vibration for an additional hour to remove any remaining or dissolved air bubbles from the solution.
g. The dilatometer is placed back inside the water bath at the target temperature.
h. The tower is wrapped with insulation in order to minimize condensation effects inside the tower.
i. LVDT movement due to initial thermal expansion followed by ASR is recorded by a data acquisition system.

Table 1 Dilatometer test procedure.

Step	Time (hours)	Temp.	Purpose/Process
Aggregate (oven dry) immersion in selected alkaline solution	12-14	23°C	Saturation of aggregate pore system (easily accessible pores)
First Vacuum (Aggregate + solution) under vibration	2-3	23°C	Removing air bubbles from solution as well as saturation of unsaturated pores (hard to saturate by immersion alone in the previous step)
Preheating dilatometer in water bath	1.5-2	Target	Heat the dilatometer to target temperature
Second vacuum (Aggregate + solution) under vibration	1	Target	Further pore saturation due to thermal expansion effects
The LVDT movement due to thermal expansion	3-4	Target	Assigning a reference LVDT reading at stable target temperature
LVDT movement due to ASR	55-60	Target	Recording volume change due to ASR

The test duration was arbitrarily selected as 3 days. However, it can be run for longer periods, if desired. The exact length of test period has not been established yet. Additional research is required to determine this criterion.
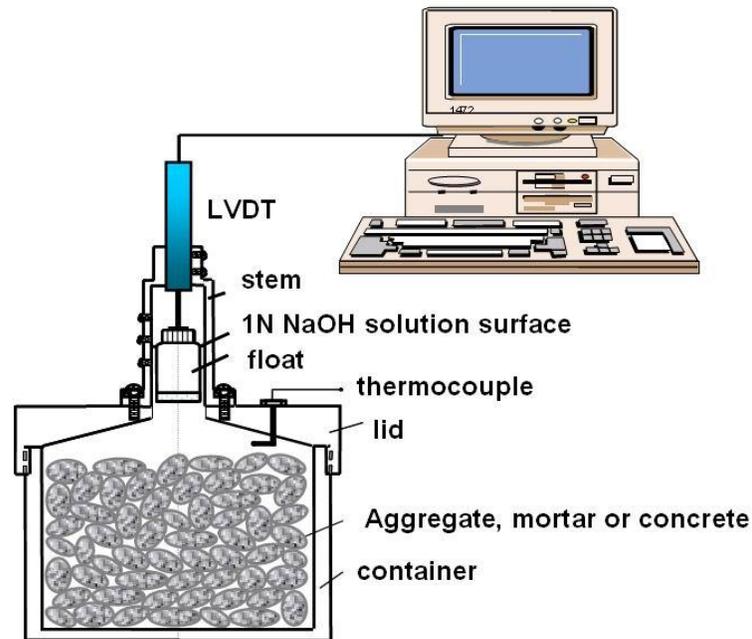
Figure 6 A cross sectional view of the dilatometer with the float at the top.

Calculation of ASR Expansion

The calculation of volume change of the tested aggregate because of ASR is as follows:

$$E_a(\%) = \frac{\Delta V_{ASR}}{V_{Aggregate}} \times 100$$
$$\Delta V_{ASR} = A_{Tower} \times \Delta H$$

where:

$E_a(\%)$	=	Percent expansion at n hours
$V_{Aggregate}$	=	Initial volume of aggregate
ΔV_{ASR}	=	Volume change of aggregate due to ASR at n hours
A_{Tower}	=	Surface area of the dilatometer tower
ΔH	=	Net displacement due to ASR

Data Analysis

The data is analyzed to determine fundamental material properties based on the degree of

fit of known trends of ASR expansion over time. This known trend was modeled using appropriate mathematical expressions to achieve the best fit possible. The rate of expansion (which leads to the determination of rate constant, k_T) was represented linearly over time. For the studied aggregates, 2-3 days test duration was found to be adequate to obtain representative ASR material properties (e.g., ultimate expansion, activation energy etc.).

TEST RESULTS AND DISCUSSION

Expansion Characteristics

Figures 7 through 10 show the expansion test results for the opal, jasper, flint, and chalcedony at 1N NaOH solution and three different temperatures (i.e., 60°C, 70°C, and 80°C). Low initial expansion (up to 5-10 hours) followed by a rapid increase of expansion is the overall expansion characteristics of the four tested minerals. Interestingly, the mineral opal shows lower expansion than that of other three minerals up to 10 hours, but it shows significant expansion after 15 hours irrespective of the testing temperature. Furthermore, results show that by lowering the testing temperature to 70°C to 60°C, the amount of overall expansion decreases. The most rapid and highest expansion was observed in the opal at all the three testing temperatures.
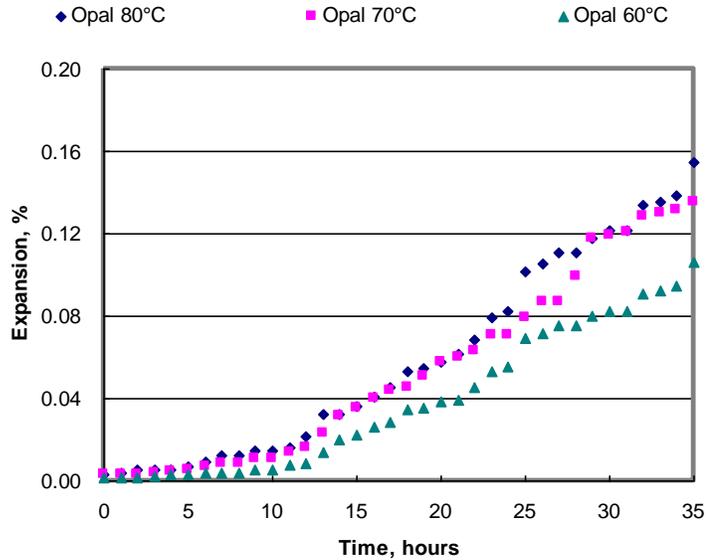

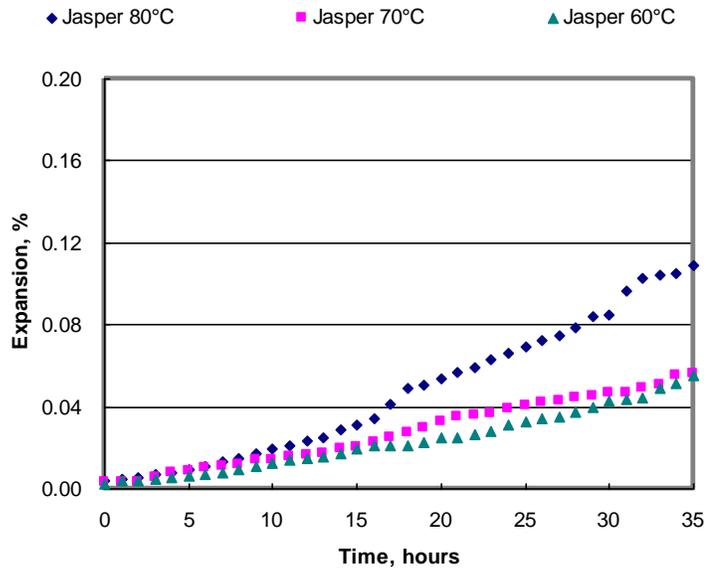Figure 7 Expansion development of opal mineral.

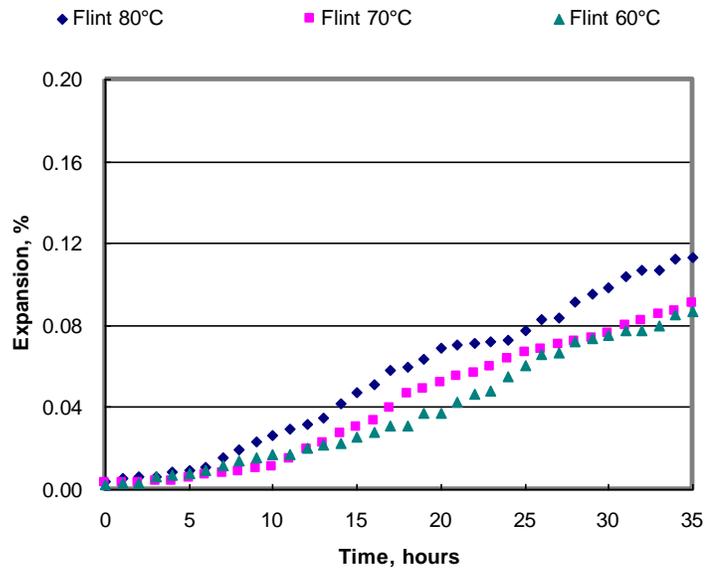Figure 8 Expansion development of jasper mineral.

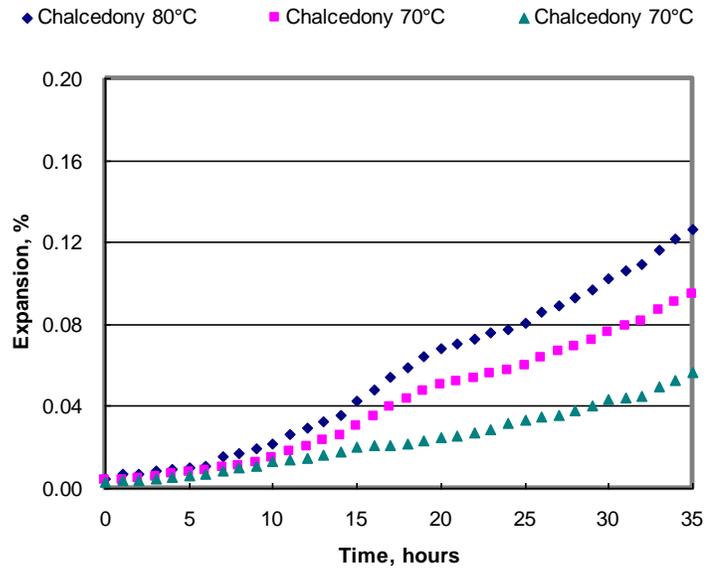

Figure 9 Expansion development of flint mineral.

Figure 10 Expansion development of chalcedony mineral.

Figures 11 and 12 show aggregate expansion results of siliceous reactive sand and New Mexico rhyolite respectively. As expected, all expansion curves display the same characteristics pattern, i.e., an initial low expansion up to 10 hours, followed by a steep rise from 10 hours to 30 hours.
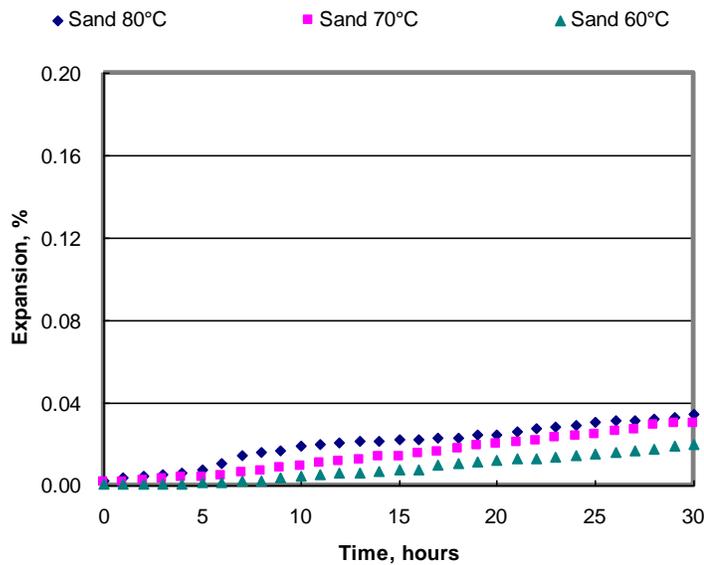

Figure 11 Expansion development of siliceous reactive sand.

These aggregates, however, produced lower expansion than that of mineral at a given temperature. It must be recognized that in this test method expansion produced due to ASR gel, not amount of soluble silica produced is measured. From these results, it emerges that this new test method can categorize minerals and aggregates based on their reactivity within a very short period of time.
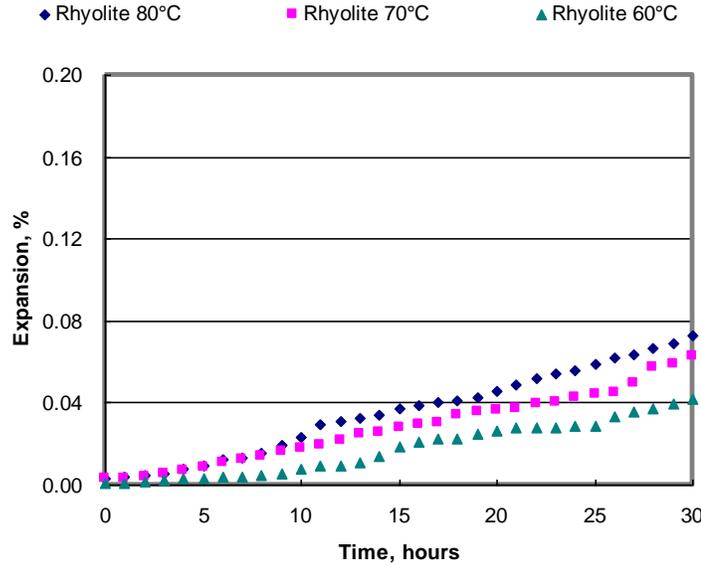

Figure 12 Expansion development of New Mexico rhyolite.

Effect of Temperature on Expansion Characteristics

Figure 13 presents the expansion values of different mineral as a function of the temperature of NaOH test solution. Three elevated temperatures were used to accelerate the reaction. The temperature of 80°C was selected to ascertain if at a later stage a correlation with expansion according to ASTM C 1260 can be established. Selection of these temperatures was arbitrary.

For all minerals, expansion increases with increasing test temperature of the test solution from 60°C to 80°C. At 80°C the expansion is higher than that at 70°C and 60°C at a given age, irrespective of mineral type. The higher amount of gel formation leads to larger overall expansion. This suggests that the increase in temperature causes increase in ASR gel formation due to high reaction kinetics. The temperature of the test solution is an important factor in the expansion characteristics of mineral.
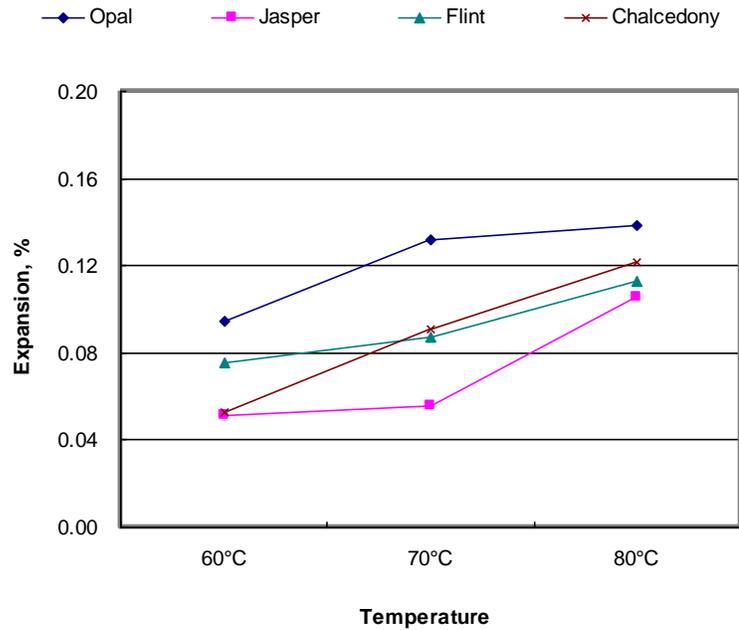
Figure 13 Expansion as a function of temperature (at 35 hours).

Reaction Products

Environmental scanning electron microscope (ESEM) was used to investigate the nature of ASR products in the tested mineral samples and is presented in figures 14, 15, 16, 17 and 18. Figures 14 and 15 show that the reaction has started on the surface and gradually progressing towards inside of an opal particle. Amorphous nature of opal is evident in Figure 16. Figure 17(a) shows that jasper is relatively coarser than opal and consists of fine crystals (cryptocrystalline). Figures 17(b) show silica dissolution with minor gel formation on a reacted Jasper particle and Figure 18 show the formation of in-situ gel. However, the overall intensity of reaction is somewhat lower in jasper than that at opal.
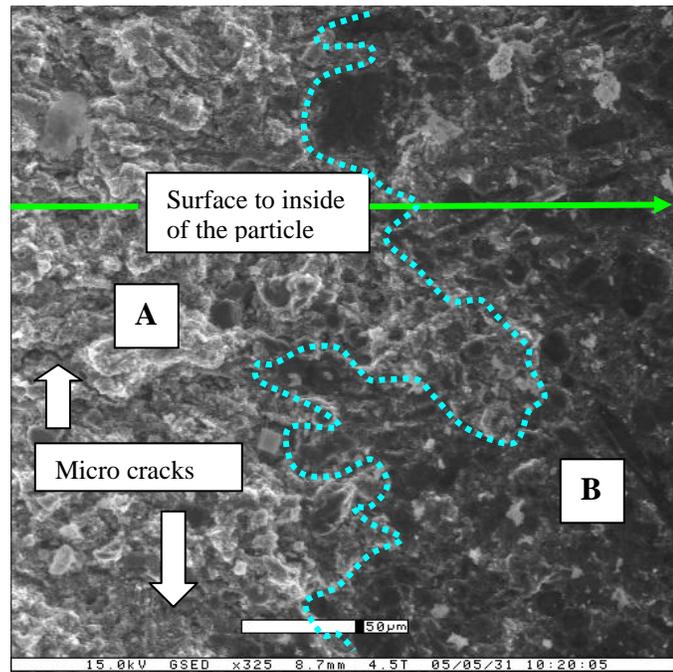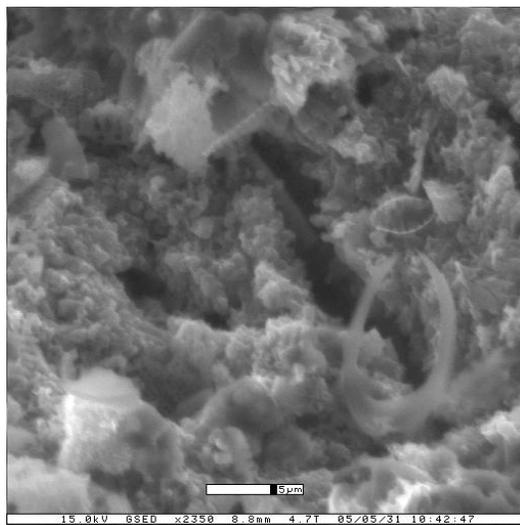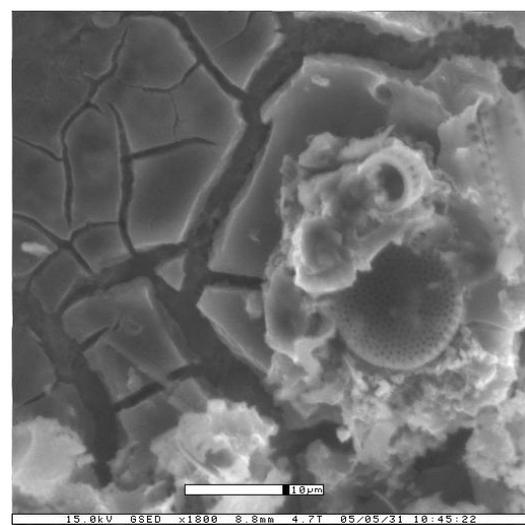
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Figure 14 Reaction front in an opal particle, A- reacted outer portion, B – Un-reacted inner portion.

(a)

(b)

Figure 15 Enlarged view of reacted portion (A) in Fig. 13. (a) In-situ gel formation through dissolution and precipitation, (b) Accumulation of gel.
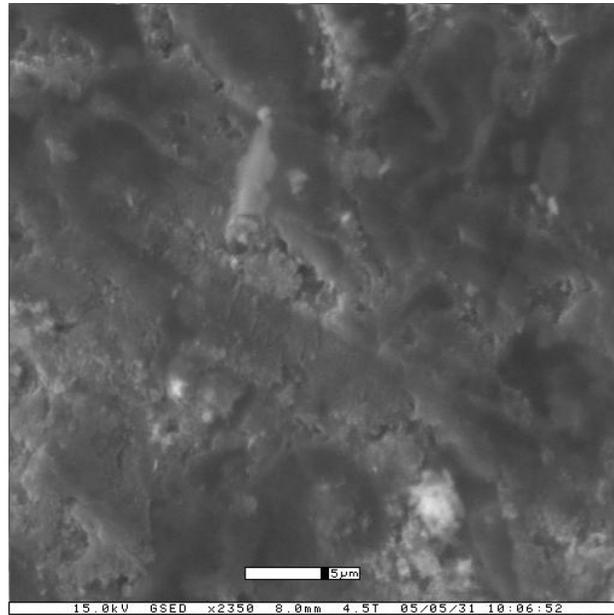
Figure 16 Enlarged view of un-reacted portion (B in Fig. 13). Note, the amorphous nature (non-crystalline) of opal.
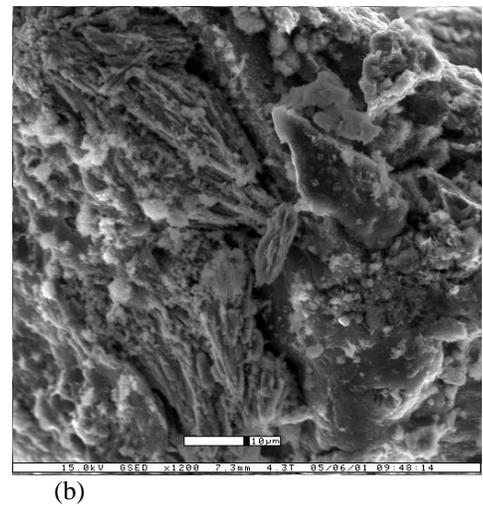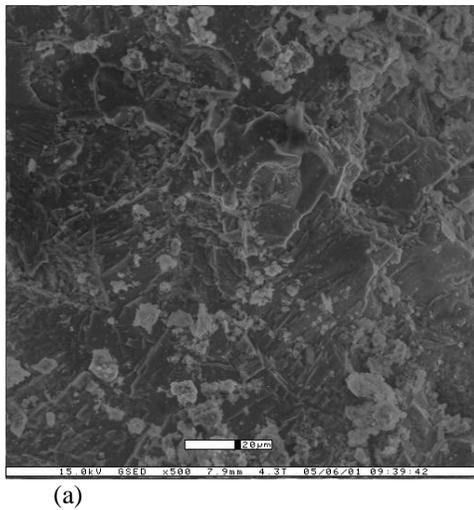

(a)

(b)

Figure 17 ASR in Jasper. (a) Un-reacted portion of a jasper particle, (b) In-situ reaction started through silica dissolution and precipitation of gel.
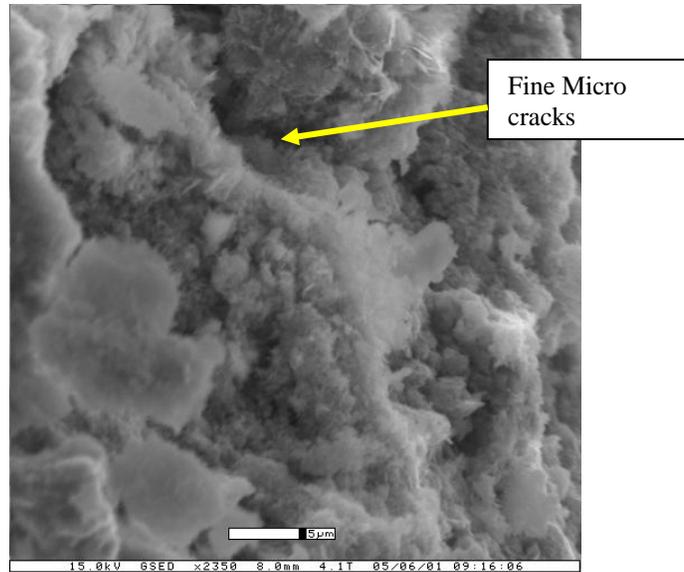
Figure 18: In-situ ASR gel in a Jasper particle

Determination of Activation Energy as a Measure of Reactivity of Minerals and Aggregates

ASR is chemical reaction that integrates the coupled effects of temperature, alkalinity, and time relative to the kinetics of ASR expansion into a single parameter. At early ages, a rise in temperature leads to an acceleration of chemical reactions between alkali and silica and hence, causes the expansion development to occur at a faster rate. This notion fits well within the concept of activation energy, which characterizes energy needed to start reaction. The use of the activation energy provides a unique parameter to evaluate ASR susceptibility of aggregate.

Activation energy was calculated from the measured time-expansion trends based on the approach described earlier. Figure 19 shows the activation energy of opal, jasper, flint, and chalcedony minerals and siliceous reactive sand and New Mexico rhyolite aggregates. The activation energy of opal (7.1 KJ/mol) is lower than that of other minerals. From the expansion behavior (Figures 7-10), it is observed that opal is more reactive (after 10 hours) than jasper, flint, and chalcedony. This is an indication that the energy needed to start ASR is comparatively low in case of mineral with high reactivity (e.g., Opal). On the other hand, the mineral with high reactivity needs less energy to initiate the reaction. From previous experience the E_a of a non-reactive siliceous aggregate has been determined to be 127.8 KJ/mol. It is important to note that opal is an amorphous form of silica whereas chalcedony, jasper and flint are cryptocrystalline forms of silica. Therefore, it is obvious that amorphous form of silica should be more reactive than the micro-crystalline or crypto-crystalline forms and it supports the results of activation energy. The reactive siliceous sand (Figure 11) consists of deformed (highly strained) crystalline quartz. It is known that strained quartz is reactive because of crystal defects imposed through

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deformation. It is to be noted that crystalline quartz without any deformation (strain) is practically non-reactive. The New Mexico rhyolite is reactive because of the presence of devitrified volcanic glass. Chalcedony and jasper are both cryptocrystalline form of silica and shows similar activation energy. It is interesting to note that flint also shows the E_a similar to jasper and chalcedony. Flint is a rock and mainly contains chalcedony. This indicates that E_a of a monomineralic rock (e.g., flint) is very similar to the activation energy of the constituent mineral (e.g., Chalcedony).

The activation energy appears to vary with the reactivity where it is greater for the aggregate than that of the mineral. From experimental results, the activation energy can be used to represent ASR potential for mineral and aggregate.
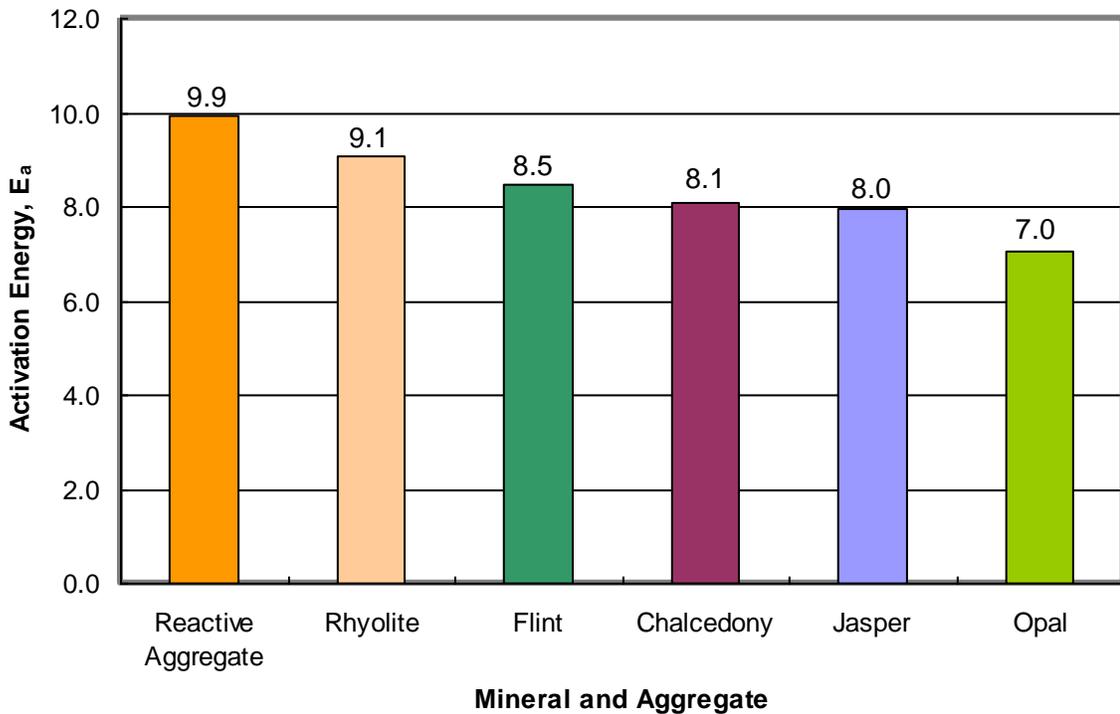

Figure 19 Activation energy of the tested silica minerals and aggregates.

Mineral E_a vs. Aggregate E_a

Alkali silica reactivity of aggregate primarily depends on the degree of reactivity of different forms of silica minerals, their nature of distribution and weight percentages. It is expected that E_a of an aggregate should be related to the E_a of the each constituent mineral in that aggregate. In earlier studies with TxDOT, dilatometer was used to measure coefficient of thermal expansion (CoTE) of pure minerals (Mukhopadhyay, 2004). A composite model was proposed to calculate aggregate CoTE based on known values of CoTE, volume percentage, and elastic modulus of each constituent mineral phase within a given aggregate (Mukhopadhyay, 2004). Just as the dilatometer testing method has been

established to measure the CoTE of aggregate as a composite of pure minerals, a similar approach may be adopted for aggregate's ASR reactivity.

Spratt limestone can be considered as an example to illustrate the E_a modeling approach. Spratt limestone contains mainly calcite with opal / chalcedony as minor minerals. The activation energy of Spratt limestone can be predicted based on the E_a of opal and calcite. If it is assumed that (i) Spratt limestone contains 15% opal and 85% calcite, (ii) the E_a of calcite is 127.8 KJ / mol (E_a of a non-reactive aggregate) and (iii) PSD of opal, calcite and limestone aggregate remain constant, then the predicted E_a of Spratt limestone would be 110 KJ/mol. But we know that sprat limestone is highly reactive and its E_a should be less than 110 KJ/mol. The next step will be to determine the actual spratt limestone E_a using dilatometer test. The predicted Ea should be adjusted by incorporating some relevant parameters in the composite model in order to match the measured dilatometer E_a. The factors (e.g., degree of crystallinity, heterogeneity etc.) responsible for E_a adjustment needs to be explored as needed in order to enhance the possibility that a aggregate model for E_a can be formulated. The different aggregates with varying reactivity will be tested for their activation energy under the project IPRF-G-002-03-2. This will provide research team a scope to formulate a modeling or a protocol approach (if possible) for the aggregate E_a as a function of such factor as E_a of constituent minerals, with respect to the degree of crystallinity, and others.

SUMMARY

Using the dilatometer to measure ASR volume expansion of mineral and aggregate represents an entirely new approach. In this study, determination of alkali silica reactivity of minerals and aggregates as a function of temperature, time, and alkalinity was attempted using dilatometer. The results indicate that the concept of activation energy can be used to represent the reactivity of mineral and aggregate subjected to ASR. Based on the results, the following conclusion can be drawn:

1. Increasing temperature of the test solution accelerates the rate of expansion due to ASR regardless of mineral and aggregate reactivity.
2. The activation energy appears to be useful approach to categorize different form of silica minerals based on their reactivity. Degree of crystallinity of different forms of silica minerals matches with the activation energy results, i.e., the lower the energy the lower is the crystallinity (e.g., amorphous or cryptocrystalline nature) and higher is the reactivity.
3. Dilatometer test is capable to determine the ASR potential of mineral / aggregate in terms of activation energy within a short period of time (e.g., 2-3 days).
4. The E_a of different forms of silica will be very useful to validate the E_a of different aggregates containing those minerals in different proportions.

The work described in this study was based on 1N NaOH test solution and limited particle size of mineral and aggregate. It may be a more realistic approach to test every mineral and aggregate using three different levels of alkalinity in order to determine a threshold alkali

level for a particular mineral / aggregate. Furthermore, size effects of mineral and aggregate also need to be considered in order to interpret the testing results.

As an additional note, it was estimated that around 10-12 kg of each mineral is necessary to complete all tests for mineral activation energy using the existing dilatometer. No suppliers were found after an intensive search to supply the needed quantity of the silica minerals. CANMET send us some mineral specimens but they were too small for testing. The non-availability of the pure minerals in sufficient quantity necessitated re-design of three small dilatometers.

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