Characterization and Modeling of Alkali-Silica Reaction of Reactive Siliceous Materials in Conducting Model and Mortar

Experiments

Lalita BAINGAM
Candidate for the Degree of Doctor
Supervisor: Professor Toyoharu NAWA
Division of Sustainable Resources Engineering

Introduction

The use of certain aggregate in harden concrete may cause in a particular chemical process in which various silica forms of aggregate react with alkali hydroxides dissolved in the pore solution of concrete, attributing to the alkali silica reaction (ASR). The ASR can produce hydrous calcium-alkali silicate and alkali-silicate gels. This so-called ASR gel absorbs water and the resulting swelling expansion, causes cracks in the aggregate grains and in the surrounding cement paste matrix leading to loss of strength and reductions in the elastic modulus and durability of the concrete. Therefore, ASR is a major liability for the durability of concrete structures. The expansion process simultaneously occurs due to the formation of gel by the ASR reaction.

However, the ASR mechanism remains unclear because some products of ASR do not produce the deleterious expansion. Recent theory related to the first aspect detailed that, when reactive silica is in contact with strong alkali ions including K, Na, and Ca ions, the ASR reaction occurs spontaneously, generating an ASR gel, acting like a phase that is possibly congruent to Ca-rich ASR gel, at the boundary of the reactive aggregate. Ichikawa and Miura proposed that the existence of a semi-permeable rigid reaction rim is generated from the reaction of Ca ions, and covers the ASR-affected aggregate, resulting in enough expansive pressure which can be eventually generated to crack the aggregate as well as the surrounding cement paste. Moreover, a reaction rim consisting of calcium-rich silica gel at the aggregate-cement paste interface of reactive aggregate has “banding” effect, which obviously prevent ASR-related expansion until the critical pressure on cracking. Therefore, there is no general agreement that calcium-rich ASR gel generates either more or less ASR-related expansion in concrete. One way to better understand the mechanism is to analyze the compositions and structure of ASR products.

As mentioned above, the expansion process occurs due to the formation of gel by the ASR reaction. The main factors that contribute to the ASR formation are reactive aggregate, highly alkaline conditions, and the moisture content in the pore solution. In particular, the aggregate used has a strong influence on the swelling mechanism generated by the reactions. This is because with reactive aggregate free silica is easily dissociated in the pore solution by the activity of hydroxide (OH\(^-\)). Highly reactive compounds tend to result in making more silica available for the ASR reaction. It is accepted that ASR is a chemical reaction which is highly sensitive to temperature. Thus, a rise in temperature may be considered to be involved in increases in the dissolution rate of soluble silica. With more silica available in the pore solution then results in greater amounts of ASR product that in turn may induce expansion by water absorption, due to the swelling characteristics of the gel. It may be deduced that the rate of expansion due to ASR depends on both the contents of ASR as well as on the capacity available for swelling.
of the gel. A study to determine the relation of expansion due to ASR to the degree of reaction has been reported. The use of SEM image analysis showed that for potentially reactive ASR, the degree of reaction of aggregate is around 12%. Approximately 5% of the degree of reaction is classified as non-deleterious aggregate. Buteel et al. developed a chemical method for quantitative characterization of ASR by considering two reaction degrees: the number of moles generated by siloxane bond break up inside the aggregate and the number of moles of monomers and small polymers obtained from dissolution. Additionally, the reported activation energy of reactive flint aggregate is approximately 78 kJ/mol. This activation energy value is close to the activation energy breaking siloxane bonds, which would be the limiting step of the dissolution process. The rate of dissolution of soluble silica is an important factor in the ASR reaction and is related to the ambient temperature. Based on this, it may be assumed that at high temperatures, this condition accelerates the ASR, yielding more ASR gel in the pore solution and causing significant expansion. However, few studies have focused on the relationship between the dissolution rate of soluble silica and expansion behaviors due to ASR.

The present work is a part of laboratory program, which aims to establish the model system to simulate the ASR formation in concrete with accelerating conditions at highly alkaline and temperature. Four siliceous samples including Pyrex glass (PG), Yoro-chert (Yo), Seto-chert (Se) and Silica sand (SS) were investigated. The experiments describe the results of ASR generated through a reactive system conducted to gain a more comprehensive understanding of the ASR mechanism of formation and the role of Ca on ASR formation by an analysis of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Diffraction (XRD), Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM/EDX), $^{29}$Si Nuclear Magnetic Resonance ($^{29}$Si-NMR) analysis and Electron Probe Micro-Analyzer (EPMA). Correlating these experimental data with previous studies leads to insight into the sequence of reaction, particularly the ASR formation in the presence of calcium hydroxide. The sequence of the ASR can be demonstrated to divide into 4 steps, which is relevant to the species predicted to be formed by ASR, including C-S-H, C-Na-S-H, and Na-S-H suggested by the PHREEQC program. With ICP-AES, the silica dissolution at different temperatures of PG, Yo, Se and SS can be determined. From the temperature dependence of the dissolution rate, the constant rate of dissolution, the dissolution rate of soluble silica, and the activation energy ($E_a$) at any temperature can be estimated on the basis of the Arrhenius law. This comprehensive effort has been developed to take understanding of the relationship between dissolution rate of soluble silica and expansion behaviors of mortars containing ASR-reactive materials.

**Materials and Experiments**

Four silica materials were focused in this investigation. As reactive silica aggregates, two aggregates, Yoro-chert (Yo) and Seto-chert (Se) aggregates were used. Both aggregates are composed of sedimentary rocks, which had be deposited in middle-paleozoic strata, produced from the Gifu Prefecture and Aichi Prefecture in Japan, respectively. Pyrex glass (PG) produced by Iwaki Company and Silica sand (SS) was selected as highly reactive silica and non-reactive aggregate, respectively.

- **Model system**

The experimental procedure in a model system was adapted from previous work. In a model system, the reaction of materials was observed using siliceous aggregates, portlandite (CH) and 1 M NaOH (NH). 1 M NH plays the role of the pore solution and CH acts as source for calcium in hardened mortar and concrete. The aggregates were primarily grounded and sieved to a range of particle sizes from 500 to 150 μm. When 1.54 g of CH was added, CH solid was mixed gently with the aggregate samples of 5.0 g. Then 1 M-NH solution was
added to the samples in the aggregate/solution ratio of 0.25 and immediately mixed well for 3 h by magnetic stirrer. The samples were separated into several-30 mL polyethylene tubes and placed in an oven at high temperatures (60, 70 and 80°C) to accelerate reactions. The reaction was stopped at 24, 72, 120, 168, 240, 336, 480 and 576 h for the mixtures with 1 M-NH by filtration through a 0.45-µm filter and washing the solid with acetone to stop the reactions. In case of rapidly reactive glass, the reaction was shorten to stop at 3, 7, 14, 24, 72, 120 and 168 h for PG mixtures. In an attempt to seek the effect of Ca on ASR formation, the fine chert (a range of particle sizes from 300 to 150 μm) of 5.0 g was also mixed with small amounts of CH solid of 0.77 and 0.385 g. For the sake of simplicity, only the Yo-chert was selected (Yo+NH+CH_0.77 and Yo+NH+CH_0.385). By doing these mixtures, we were able to simulate the reaction environment that CH was almost consumed. After being placed in the oven at 80°C for 14 days, the samples were kept as the same method as mentioned previously.

Solids were placed in an oven at 40 °C until they were dehydrated and then were provided for XRD, SEM-EDX and 29Si-NMR. All samples were filtrated by 0.45 µm filter at 24, 72, 120, 168, 240, 336, 480 and 576 h for Se, Yo and SS, and at 3, 7, 14, 24, 72, 120 and 168 h for PG and washing the solid with acetone solution to stop the reactions. Liquid samples were diluted to the range from 10 ppb to 10 ppm of the Si concentration and then the dissolved Si content in the liquid samples was quantified by ICP-AES. The activation energy (E_a) of soluble silica from each material can be calculated on the basis of Arrhenius equation.

**Simulation of Phase Assemblage**

The PHREEQC is used for calculations of hydrogeochemistry and is a useful tool for modeling data. The results of geochemical evaluations depend on factors like the quality of the input data and the sequence of the calculations. For the simulations, the phase-equilibrium were built in the program and the input data were followed by ion concentrations to determine the ion activities and the relevant states for the involved minerals to precipitate as ASR product, including tobermorite type C-S-H, in this investigation. ASR phase is defined by chemical reactions, an equilibrium constant.

**ASR-induced expansion of mortar**

Pyrex glass (PG) and silica sand (SS) were crushed to the obtain particle sizes specified in ASTM C227 except for the size of the mortar bar. A white Portland cement with an equivalent Na_2O content of 3.94 kg/m³ (0.6%) was used for the mixture of mortar bar test. The mortars were prepared in prismatic specimens of 2.8x2.8x18.0 cm for PG and SS. The water-cement (w/c) ratio of the mortar was 0.50 and the sand to cement ratio 2.25. After demolding, the mortar prisms were kept in a sealed container at 40°C. At each measurement (at 7, 14, 21, 28 and 56 days), the sizes of the mortars were determined using a length comparator with the scale millimeter method.

**EPMA Analysis of Mortar-bar**

In microstructure examination, the EPMA was chosen to perform on our mortar prisms. With EPMA analysis, the Ca/Si ratio of ASR product can be identified. The mortars of SS100 and PG100 with 1.2% alkali were selected and cut into a small size of 1.0x1.0 cm. Samples were arranged in the mold and then molded with Specifix-20 resin. After demolding, the samples were placed in an oven at 40°C for 3 days. Fig. 3.3 shows the sample preparation provided for EPMA analysis. Especially for high magnification, the samples were polished with sand paper and diamond slurry to be a smooth surface and then coated with carbon. Field Emission Probe Micro Analysis, EPMA with a model of JXA-8530F (JEOL manufacture, Japan), was conducted with an acceleration voltage of 15.0 kV.

**Results and Discussion**

**Ion concentrations determined by ICP-AES**

The considerable contents of soluble silica (SiO₂) in the four samples up to 24 days were determined. For
example, **Fig. 1** show the content of SiO$_2$ of liquid sample-Pg in the presence and absence of CH for 3 temperatures (60, 70 and 80°C). With CH, there were low contents of SiO$_2$ and quite different from the dissolved Si of liquid samples without CH. These changes suggest that the rate of Si dissolution may be related to the available Ca ions. At the initial stage, dissolved hydrous silicate ions such as Si(OH)$_2$$^-$ may react with Ca ions and result in the formation of calcium silicate hydrate, C-S-H, which does not have a constant composition but rather that the composition depends on the activity of the Ca ions. These results suggest that after most of the Ca ions are consumed the rate of Si dissolution increases.

**Fig. 1** Concentration of soluble silica in liquid samples

- **XRD, $^{29}$Si-NMR and SEM/EDX results of insoluble products (Model system at 70 and 80°C)**

There are no significant spectra in the powder samples without CH. In the presence of CH (**Fig. 2**), the XRD patterns conducted under temperature 80°C of both Yo+NH+CH and Se+NH+CH show peak patterns at 7.14°2θ and 29.34°2θ which changes with reaction time, indicating ASR product incorporation with Ca. The $^{29}$Si-NMR peaks at -79 and -85 ppm in the solids of Yo+NH+CH at 3 days of reaction, represent Q$^1$ and Q$^2$ sites, respectively. The relative intensity of the -85 ppm (Q$^2$) peak increased until 14 days of reaction in support of a process of polymerization of ASR product. With CH present, the peaks at -79 (Q$^1$) and -85 (Q$^2$) ppm of ASR are associated with the chemical structure of C-S-H which is dominated by Q$^1$ and Q$^2$ sites in the $^{29}$Si-NMR spectra. In an attempt to verify the effect of Ca ions on ASR formation, the XRD results of Yo+NH+CH 0.77 and Yo+NH+CH 0.385 displayed the significantly broadened peak located 30°2θ. The $^{29}$Si-NMR spectra reveals that not only the Q$^1$ (-79 ppm) and Q$^2$ (-85 ppm) sites were detected, the relative intensity of -95 ppm (Q$^3$ sites in the range from -91 to -98 ppm was expected in OH$^−$ and Na$^+$ containing system) was apparently observed in both Yo+NH+CH 0.77 and Yo+NH+CH 0.385 at 14 days of reaction. It is believed that excessive alkali ions might be incorporated into the re-polymerization of tobermorite type C-S-H to produce ASR, such as C-Na-S-H. Addition to the SEM with EDX analysis (SEM/EDX), the value of Ca/Si ratios can be roughly estimated: 0.74 for Yo+NH+CH and 0.81 for Se+NH+CH. The value is similar to Ca/Si ratio of 0.83 for tobermorite type C-S-H. Taking into account that a value of Ca/Si ratio of produced C-S-H was not a define value but distributed, SEM/EDX observations confirms that reacted samples at 14 days of Yo+NH+CH and Se+NH+CH include tobermorite type C-S-H.

**Fig. 2** XRD patterns of Yo+NH+CH and Se+NH+CH solids. The notations “G” and “CH” are the ASR phase and the portlandite phase.

For accelerating condition of model system at 70°C, there are no broad peaks for amorphous and poorly-ordered crystalline silicate in the powder samples of Yo+NH (70 °C) and PG+NH (70°C).
Whereas the XRD peaks of Yo+NH+CH (70°C) and PG+NH+CH (70°C) at 29.4°20 became sharper with the progress of the experiment. Addition to 29Si-NMR spectra of Yo+NH+CH (70°C), there are main peaks at -78.8 ppm (the end chain tetrahedral Q1) and -84.1 ppm (non-bridging tetrahedral Q2) in Fig. 3. At 336 h, the intensity of Q2 has increased and become dominant (the Q1/Q2 ratio < 0.50). At the end of the experiments at 576 h there were Q1, Q2, and Q3 sites, and it appears that the chemical shift of the signal was initially dominated by Q1 when there were Ca ions present in the solution. Moreover, the spectra of PG+NH+CH (70°C) shows initial peaks at -79.9 ppm (the end chain tetrahedral Q1) and -84.1 ppm (non-bridging tetrahedral Q2). After 24 h, the major peak of the Q2 site was alone, suggesting the formation of additional Na-rich product (Na-S-H). These results indicate the effect of Ca ions on the structure of the product that is related to the sequence of ASR.

![Fig. 3 The 29Si-NMR results of Yo+NH (70°C) and Yo+NH+CH (70°C)](image)

- **Simulation of Phase Assemblage by PHREEQC**

The sequence of ASR of chert-aggregate can be demonstrated on the basis of thermodynamic equilibrium model using XRD 29Si-NMR and SEM/EDX data. The overall stages of the ASR process for chert-aggregate can be divided into 4 steps: (i) formation of a stable C–S–H_0.83 by reaction between dissolved Si ions from chert and Ca ions; (ii) after complete consumption of CH, formation of C–Na–S–H by reaction between existing C–S–H, Na ions, and dissolved Si ions; (iii) during the conversion of C–S–H to C–Na–S–H, the Si concentration in the solution keeps increasing; (iv) following (iii) there is formation of Na–S–H by reaction between dissolved Si ions from chert and alkali ions.

![Fig. 4 Plot of experimental and simulated data of PG](image)

For reactive glass material, the predicted species of ASR including C–S–H_1.66, C–Na–S–H, and Na–S–H and the ion concentrations remaining in the solution of PG + NH + CH, as shown in Fig. 4. The sequence in the simulated process of ASR can be divided into 4 steps and the simulation model tends to give predictions of C-S-H, C–Na–S–H, and Na-S-H that are in agreement with the experimental data from the corresponding tests, as mentioned previously in the XRD and 29Si-NMR results. Hence our simulation strongly confirms that sequence of the ASR of PG is the same as those of both cherts (Yo and Se). This also suggests that the ASR examination using PG can be used for and would be effective to understand the chemical and physical
behavior of the ASR induced expansion of mortar and concrete.

- **ASR-induced expansion of mortar**
  The alkali content of the mortar mixtures has a significant effect on ASR, and mortars with two alkali contents (equivalent Na₂O) of 3.94 (0.6%) and 7.27 kg/m³ (1.2%) were investigated. With the low alkali content of 0.6%, there is no appreciable expansion in either of SS100 or PG100 (marks with solid lines). In Fig. 5, the notations of mortars containing SS and PG mixed with 1.2% alkali are represented by SS100 (circle marks with dash line) and PG100 (triangle marks with dash line), accordingly. With the alkali content adjusted to 1.2%, the SS100 still showed only a low expansion of 0.016%. Only the expansion of the PG100 showed significant expansion. At 56 days of exposure, the expansion of PG100 had increased to 0.55%. These results allow the conclusion that PG is a highly reactive compound inducing expansion due to ASR.

In the EPMA analysis, the locations of ASR gel can be identified such as in the cracked aggregate (the Ca/Si ratios < 0.5, red cross) or in the rim near the reactive site (the Ca/Si ratios > 0.5, blue cross), as shown in Fig. 6. This result is linked to Katayama that ASR with Ca/Si ratios less than 1.00 mostly deposited in the cracked aggregate, while ASR in the cement paste has been found to be high Ca/Si ratios (0.50-1.50).

- **Rate of dissolution of silica in model system and its contribution to ASR-induced expansion of mortar under temperature of 40 °C**
  As investigated in model system corresponding to simulation data, the C-S-H_1.66 existed in PG samples. With high dissolution rate of silica, that respects to Ca consumption, producing the greater amount of C-N-S-H. This contributes to significant expansion by PG mortar. It is believed that high content of C-N-S-H found in PG sample seem to be metastable phase that is responsible for essential swelling of gel.