A Numerical Model for Chemical Kinetics of Alkali Silica Reaction in the Closed Reactive System

Taehwan Kim [1] and Jan Olek[1]
[1] Purdue University, School of Civil Engineering
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Background

- The deterioration induced by alkali silica reaction (ASR) is initiated by complicated heterogeneous chemical reactions.
- The reaction products imbibe water and exert pressure on the surrounding paste and aggregate.
- Existing ASR models: Poyet, et al. [1], Bažant and Steffens [2], Multon, et al. [3] and Ulm, et al. [4]
- Most of these models typically oversimplify the chemical side of ASR process.

[1] S. Poyet, A. Sellier, B. Capra, G. Foray, J. M. Torrenti, H. Cognon and E. Bourdarot, Chemical modelling of Alkali Silica reaction: Influence of the reactive aggregate size distribution, Materials and Structures, 40, 2007, pp. 229-239
[2] Z. P. Bažant and Alexander Steffens, Mathematical model for kinetics of alkali-silica reaction in concrete , Cement and Concrete Research, 30, 2000, pp. 419-428
[3] S. Multon, A. Sellier and M. Cyr, Chemo-mechanical modeling for prediction of alkali silica reaction (ASR) expansion, Cement and Concrete Research, 39, 2009, pp. 490-500
[4] F.J. Ulm, O. Coussy, L. Kefei and C. Larive, Thermo-Chemo-Mechanics of ASR Expansion in Concrete Strutures, Journal of Engineering Mechanics, 126, 2000, pp. 233-242

Objectives

To demonstrate the application of the geochemical modeling to simulate the chemical process of ASR in the closed reactive system (reactor system).

- Part I: Formulation of the kinetic rate law for dissolution of silica from the reactive silica minerals.
- Part II: Simulation of the ASR process using the developed kinetic rate law and the commercial geochemical modeling software (Geochemist's Workbench® (GWB))

Assumptions

- The ASR process taking place in the reactor method is the surface-controlled reaction between the solution and the exposed surface of reactive silica
- The reaction sequence assumed in the ASR model is the same as that observed during the experiments

Formulation of Kinetic Rate Law

- Silica dissolution reaction: $SiO_2 + 2OH^- \rightleftarrows H_2SiO_4^{2-}$
- pH dependence: $k_\theta \propto (a_{OH^-})^{n_\theta}$
- Temperature dependence: $k_\theta = Ae^{-E_\theta / RT_K}$
- The influence of electrolytes: $k_\theta \propto (I)^{0.2}$

↓

- Rate of silica dissolution

$$r_\theta|_{diss} = A_\theta k_\theta = A_\theta k_+ (a_{OH^-})^{n_\theta} (I)^{0.2}$$
$$k_+ = A_+ e^{-E_\theta / RT_K}$$

Transition state theory

↓

- The net rate of dissolution of silica

$$r_\theta|_{net} = -\frac{dn_{SiO_2}}{dt} = A_\theta k_+ (a_{OH^-})^{n_\theta} (I)^{0.2} \left(1 - \frac{Q}{K_{eq}}\right)$$

Flow Chart for the Development of the Model

Numerical Modeling (GWB Software)

Formulation of Kinetic Rate Law

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Framework for the ASR Process
- Three major products (C-S-H, C-S-H(A) and A-S-H)
- C-S-H: 1.4nm tobermorite ($Ca_5Si_6H_{21}O_{27.5}$)
- C-S-H(A): $K_2Ca_4Si_6H_{21}O_{27.5}$ or $Na_2Ca_4Si_6H_{21}O_{27.5}$
- A-S-H: kanemite ($KHSi_2O_5 \cdot 3H_2O$ or $NaHSi_2O_5 \cdot 3H_2O$)

↓

Input data	Parameters
• Concentrations • Amount of water • Amount of $Ca(OH)_2$ • Amount of silica mineral • Temperatures	• Surface area (A_θ) • Activation energy (E_θ) • Pre-exponential factor (A_+) • Coefficient (n_θ) • Thermodynamic properties of products

Adjusted during calibration

↓

GWB Simulation of Reactor Experiment
- Mass action equation and mass balance equations
- Newton-Raphson iteration method

↓

Results of Simulation

↓

Comparable?

No → **Calibration (Adjustment of Parameters)** → Formulation of Kinetic Rate Law

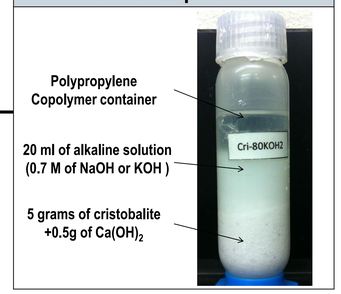
Yes ↓

Analysis of the results from model and experiments

Experiments of Closed Reactive System (Reactor Experiment)

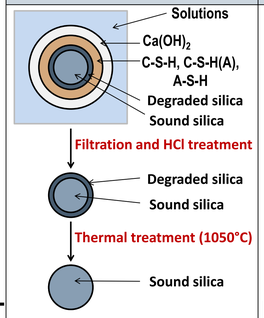
BET
- Nitrogen Absorption
- Surface Area of Cristobalite

Reactor Experiment



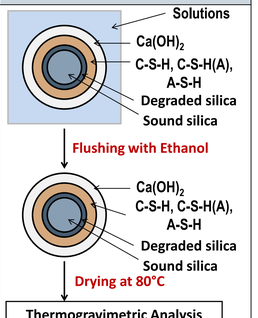
Series of Experiments
- Different alkali solutions (NaOH or KOH – 0.7M)
- Different temperatures (38°C, 55°C and 80°C)
- Different exposure times (from 1 hour to 30 days)

Acid Treatment



Outcomes
- Changes in concentrations of solution (ICP-OES)
- Amount of dissolved silica
- Amount of degraded silica
- Amount of sound silica

Alkaline Treatment



Outcomes
- Changes in concentrations of solution (ICP-OES)
- Amount of $Ca(OH)_2$

Mass action equation

$$K_j = \frac{a_w^{\nu_{wj}} \cdot \prod^{i} (\gamma_i m_i)^{\nu_{ij}} \cdot \prod^{k} a_k^{\nu_{kj}}}{\gamma_j m_j}$$

Mass balance equation

$$M_w|_t = n_w \left(55.5 + \sum_j \nu_{wj} m_j\right)$$

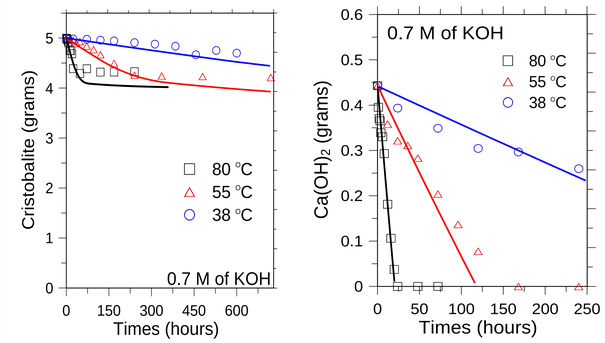
$$M_k|_t = n_k + n_w \sum_j \nu_{kj} m_j$$

$$M_i|_t = n_w \left(m_i + \sum_j \nu_{ij} m_j\right), \text{ where } i = Na^+ \text{ or } K^+$$

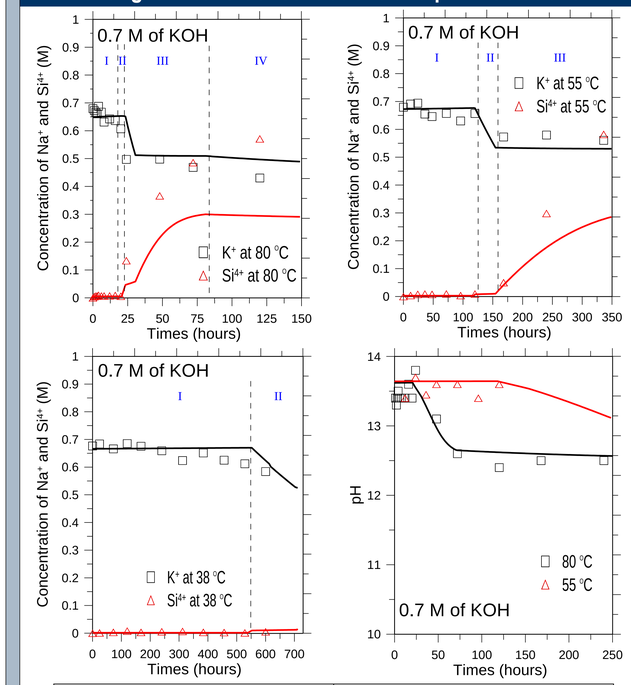
$$M_i|_{t=0} + \int_0^t r_\theta|_{net}(t)dt = n_w \left(m_i + \sum_j \nu_{ij} m_j\right), \text{ where } i = H_2SiO_4^{2-}$$

$$M_i|_{t=0} - 2\int_0^t r_\theta|_{net}(t)dt = n_w \left(m_i + \sum_j \nu_{ij} m_j\right), \text{ where } i = OH^-$$

Dissolution of Cristobalite and Consumption of $Ca(OH)_2$



Changes in Ions Concentrations and pH in Solutions



Stage I: Formation of C-S-H	Stage III: Increase in Si^{4+} conc.
Stage II: Formation of C-S-H(A)	Stage IV: Formation of A-S-H

Conclusions

- In general, there appears to be a good agreement between the modeling results and the experimental results.
- The proposed process of ASR gel formation is very similar to the processes reported in the literature [1, 2].
- Combining the experimental results and the modeling results helped to develop the understanding of the chemical reaction process of the formation of ASR gels.

[1] Hou, X, Kirkpatric, R.J., Struble, l.J and Monteiro, P.J.M., Structrual Investigation of Alkali Silica Gels, Journal of American Ceramic Society, 88, 2005, pp. 943-949
[2] Hou, X., Struble, L.J. and Kirkpatric, R.J., Formation of ASR gel and the roles of C-S-H and portlandite, Cement and Concrete Research, 34, 2004, pp. 1683-1696