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Model of ion transport in alkali-activated materials

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Summary: *The paper deals with simulation of* Na^+ *leaching process occurring in alkali activated fly ashes (AAFA). The motivation arose from the concern of efflorescence, occurring in a moisture-gradient environment in these materials. The objective aims at quantification of unknown diffusion coefficient for* Na^+ *and estimation of time-dependent leaching process. Numerical model formulated for 1D and 3D is used to solve the balance equation. The 1D model was created in Matlab/Octave environment and the 3D model was implemented into in-house OOFEM package. The simulation shows feasibility of proposed models and a good correspondence with experimental data.*

1. Introduction

Application of alkali-activated fly ash can, hopefully in a near future, replace partially ordinary Portland-based concrete. Production of 1 ton of Portland cement releases almost additional 1 ton of CO_2. On the other hand, worldwide production of fly ash is enormous environmental burden, arising from coal burning process in power stations. It is estimated that 800 millions tons of fly ashes are produced solely in 2010 (Jimenez & Palomo, 2005). In the Czech Republic, the production reaches about 10 millions tons of fly ashes annually. Only a small part is utilized at present (20-30%). The rest is stored on landfills which occupy large areas and bring a negligible risk of air and ground water pollution. The production of fly ash will definitely occurre in a near future due to lifetime of thermal power plants. It means that the production of fly ash will continue in the next decades at least. Due to this fact, a suitable utilization of fly ash in large quantities is searched. Economical advantage seems to play a significant role due to low cost of this waste material. Previous research testified that fly ash can enter the process of alkali-activation. Alkali-activated materials show excellent performance in acid resistance, fire resistance, low drying shrinkage, low calcium content, improved durability, no alkali-silica reaction, freeze/thaw performance or lower creep induced by mechanical load, when compared to ordinary concrete (Wallah and Rangan , 2006).

Efflorescence presents a major problem in alkali-activated materials. After the activation, significant amounts of unreacted alkalies remain in the system, which can be leached via a slow diffusion process. The rate of leaching and total amount of remaining alkalies have never been quantified before and present the main objective of this contribution. Numerical methods, particularly finite element approach, form the framework of this diffusivity simulation. The source data for the simulation came from the experiments carried out at the Institute of Chemical Technology in Prague.

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2. Differential formulation of non-stationary diffusion equation

Let us consider a 1D element with axis x, volume Ω and boundary Γ. The non-stationary diffusion problem means that the concentration $w(x,t)$ inside the element changes with a respect to time. Assuming a homogeneous isotropic material with a diffusivity λ, the differential equation reads (Z. P. Bažant & L. J. Najjar, 1972),

$$\lambda \frac{\partial^2 w(x,t)}{\partial x^2} = \frac{\partial w(x,t)}{\partial t}. \tag{1}$$

To solve Eq.(1), one needs to define boundary and initial conditions. The initial conditions define the concentration field at zero time, that means $w(x,0) = \overline{w}(x,0)$. The boundary conditions can appear in many forms, for example

- Dirichlet (or first-type) boundary condition, prescribing the concentration on the domain boundary
  $$w(x,t) = \overline{w}(x,t) \text{ on the boundary } \Gamma, \tag{2}$$
- Neumann (or second-type) boundary condition specifies the ion flux across the boundary
  $$\frac{\partial w(x,t)}{\partial t} n = \overline{\frac{\partial w(x,t)}{\partial t}} \text{ on the boundary } \Gamma, \tag{3}$$
  with outward normal n,
- supplementary boundary condition for the flux with respect to a ion transfer coefficient B at the surface given by Newton's law
  $$\frac{\partial w(x,t)}{\partial t} = B\left[w(x,t) - \overline{w}(x,t)\right] \text{ on the boundary } \Gamma, \tag{4}$$
  with a given concentration far from boundary layer $\overline{w}(x,t)$.

2.1. FEM and time discretization

The solution of Eq.(1) proceeds using the FEM. A weak form stems from the principle of zero virtual work of the concentration over the element. The solution of Eq.(1) is fulfilled only in average at the volume Ω,

$$\int_\Omega \left[\frac{\partial w(x,t)}{\partial t} - \frac{\partial w^2(x,t)}{\partial x^2}\right] \delta w(x,t) dV = 0. \tag{5}$$

To fulfill the Dirichlet condition, Eq.(2) requires $\delta T(x,t)$ on the boundary Γ to be equal to zero. Applying the Green formula on Eq.(5) yields

$$\int_\Omega \frac{\partial w(x,t)}{\partial t} \delta w dV + \int_\Gamma \overline{\frac{\partial w(x,t)}{\partial t}} \delta w dV - \int_\Omega \frac{\partial w(x,t)}{\partial t} \delta \frac{\partial w(x,t)}{\partial x} dV = 0. \tag{6}$$

Let us divide the element to finite sections with volume Ω_e and approximate linearly the concentration and flux in each finite element

$$w(x) \approx \mathbf{N}\boldsymbol{w}, \tag{7}$$

$$\boldsymbol{q} = \frac{\partial w}{\partial x} \approx \mathbf{B}\boldsymbol{w} = \frac{\mathrm{d}\mathbf{N}}{\mathrm{d}x}\boldsymbol{w}, \tag{8}$$

where $\mathbf{N}$ is a linear interpolation function and the matrix $\mathbf{B}$ contains the derivatives of the interpolation functions. The virtual vector of concentrations is approximated in the same manner. Substituting Eqs.(7 and 8) into the Eq.(6) yields the weak form,

$$\mathbf{C}\dot{\boldsymbol{w}} + \mathbf{K}\boldsymbol{w} = \boldsymbol{p}, \tag{9}$$

where the dot means time derivative and vector $\boldsymbol{p}$ includes the boundary conditions. The used matrixes are defined as

$$\begin{aligned} \mathbf{C} &= \int_\Omega \mathbf{N}^T\mathbf{N}\mathrm{d}\Omega, && (10)\\ \mathbf{K} &= \int_\Omega \mathbf{B}^T\lambda\mathbf{B}\mathrm{d}\Omega, && (11)\\ \boldsymbol{p} &= -\int_\Gamma \mathbf{N}^T\overline{\boldsymbol{q}}\mathrm{d}\Gamma. && (12) \end{aligned}$$

The time discretization approximates the nodal values $\boldsymbol{w}$ from Eq.(9) at all times using selected computed time points. The time evaluation points have a constant time difference, $t_i = i\Delta t$ for $i = 0, \ldots, T$. For the numerical integration, the parameter τ, which gives time point of derivative evaluation during the time step. $\tau = 0$ means explicit method, the derivative from Eq.(9) is approximated by the slope in a last known time step t_i. $\tau = 1$ means unconditionally-stable implicit scheme, the derivative is obtained at time t_{i+1}. $\tau = 0.5$ means the Crank-Nicolson method and the derivative is evaluated in the middle of the time step.

The final equation for the 1D simulation takes the form,

$$\left(\frac{\mathbf{C}}{\Delta t} + \tau\mathbf{K}\right)\boldsymbol{w}_{i+1} - \tau\boldsymbol{p}_{(i+1)} = \left(\frac{\mathbf{C}}{\Delta t} + \tau\mathbf{K}\right)\boldsymbol{w}_i + (1-\tau)\boldsymbol{p}_i, \tag{13}$$

where $\boldsymbol{w}_{(i+1)}$ are the unknown concentrations. All terms at the right hand side are known from last time step.

3. Simulation, results and discussion

All simulations aimed at description of Na^+ ions from alkali-activated specimens. Specimens sized $40 \times 40 \times 160$ mm were submerged into 600 ml of water for 2 weeks. The concentration of Na^+ ions in the water was measured every 24 hours.

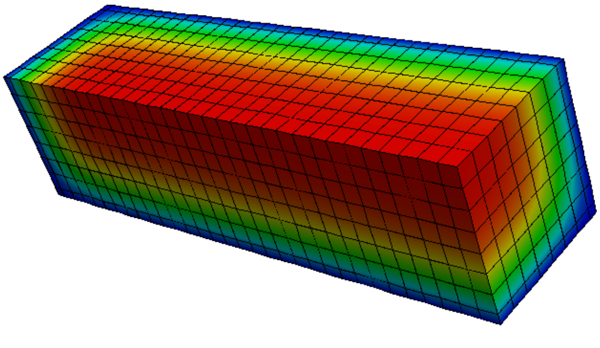

Figure 1: 3D simulation of Na^+ leaching

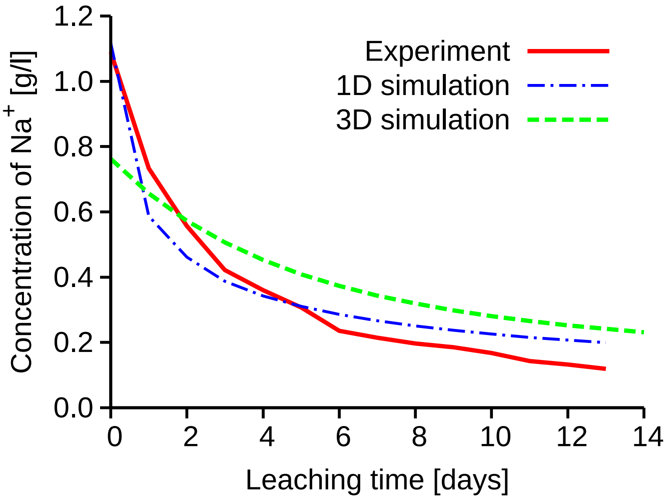

Figure 2: Leaching results from experiments and 1D and 3D simulation.

The first simulation approximated the problem with 1D elements. The length of finite elements was 20 mm (the half of the shortest sample edge dimension) with the preservation of volume. The mathematical formulation derived above was implemented into Matlab/Octave code. Unknown value of diffusion coefficient was determined as the best fit to experimental data using the method of least squares. The Fig.(3) shows the distribution of concentration inside the body in the 1D case after 14 days of leaching.

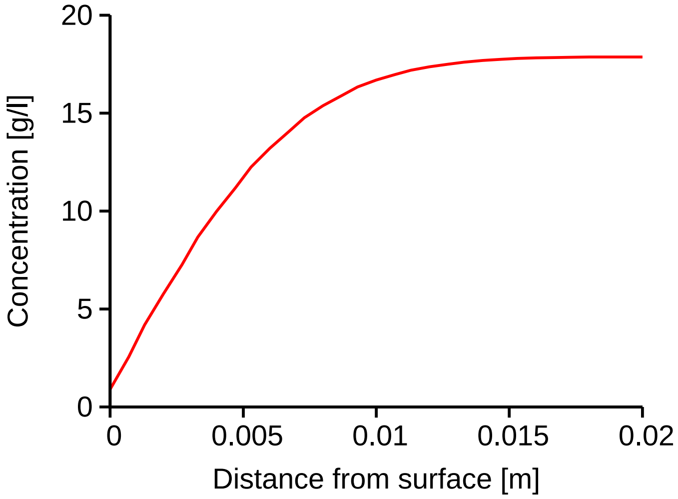

Figure 3: 1D simulation of Na^+ leaching

More advanced 3D simulation was carried out in the OOFEM code made by B. Patzák & Z. Bittnar (2001). Geometry of specimen was meshed using linear brick elements. Only 1/8 of volume was considered due to symmetry of the problem; the reduced problem was represented with 20x20x80mm prism with three free boundaries (the middle of sample) and with three prescribed boundaries (the surface of experimental sample).

Diffusion coefficient for Na^+ ions transport in the saturated state 5.7 x10^{-5} m^2/day.

4. Conclusion

The work demonstrated the successful application of numerical methods for the assessment of Na^+ diffusion coefficient. Both 1D and 3D formulations proved to give reasonable results with leaching experiments. Quantification of Na^+ diffusion coefficient is important in the prediction of efflorescence, which strongly depends on a sample geometry and moisture-gradient environment.

5. Acknowledgment

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6. References

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