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Numerical model of the alkali-silica reaction development with external source of alkalis

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Abstract

Experimental research, in which mortars prepared with reactive aggregates have been exposed to different conditions, has been performed. The samples have been stored in water or 1M NaOH water solution at 80ºC. Based on the observed strains, ASR extent has been calculated. Mathematical model of combined action of hygro-thermal, chemical and mechanical phenomena has been developed to analyze evolution of the ASR reaction. It is based on mechanics of multiphase porous media. Development of the ASR depends on the alkali content. Diffusion of alkalis from the cement paste to the aggregate grains is considered. Both external alkali sources and alkali binding by the formed ASR gel are taken into account. The proposed mathematical model has been validated by comparison with the experimental results.

1. Introduction

The alkali-silica reaction (ASR) occurs in the reactive aggregates only after reaching sufficient alkali content. Threshold alkali concentration, above which the reaction takes place, has been already examined in the past. Rivard *et al.* [1] reported that the alkali-silica reaction occurred in the experimental research at 38ºC when alkalinity of the

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pore solutions, extracted from concrete, was higher than 270 mmol/l and 250 mmol/l. Multon and Sellier [2] reported, based on the results of Kim *et al.* [3], that the threshold alkali content is higher than 325 mmol/l, 275 mmol/l, 222 mmol/l for temperature of 20ºC, 38ºC and 55ºC, respectively.

Although laboratory methods of reactivity determination are commonly used, they have been often criticized. One of the reasons for this is that alkali leaching may occur in high relative humidity [4]. This phenomenon is of particular significance for the laboratory tests, in which small specimens are stored in water or in high relative humidity. Therefore, the specimens which are defined as reactive in one test, may be identified as non-reactive in real structures or other tests.

In the present work, mathematical model describing the ASR evolution at the mesoscopic scale, taking also into account diffusion of alkalis at the macroscopic scale caused by external source of alkalis, has been proposed. In order to validate the model, experimental research, in which specimens have been stored either in NaOH water solution or water, has been performed. Based on the observed expansions, ASR extent has been calculated.

2. Experimental research

In the research, cement CEM I 42.5 N-NA has been used. Content of alkalis has been increased to 1.2% Na_2O_{eq} by addition of NaOH to the mixing water. Two mortar series have been prepared with w/c ratio equal to 0.47 and a/c ratio equal to 2.25. In mortar M1, aggregate composed mainly of quartz mica schist, quartz, marble, limestone and gneiss has been applied. Main components of the aggregate used in mortar M2 were quartz and limestone.

Mortar bars have been cast and conditioned according to the RILEM AAR-2 method [5]. After casting, the specimens of sizes 40x40x160 mm^3 have been stored under plastic sheet for one day at 20°C. Afterwards, they have been demolded and stored in the containers filled with distilled water of temperature 20°C, which have been placed in the oven at 80°C for one day. After that period, the initial measurements of length have been taken. Half of the specimens (denoted as '-R') has been stored in 1M NaOH water solution at 80°C, as it is recommended in the RILEM AAR-2 method. The other specimens have been stored in water at 80°C ('-NR'). Therefore, in the series '-R' some alkalis should diffuse from the container towards the reactive aggregates, what should accelerate reaction development. Meanwhile, in the latter specimens alkali leaching should occur at the specimens' surfaces. Ratio of volume of liquid to volume of specimens was equal to 4:1. For each series, three samples have been tested. Average strains obtained are presented in Figure 1.
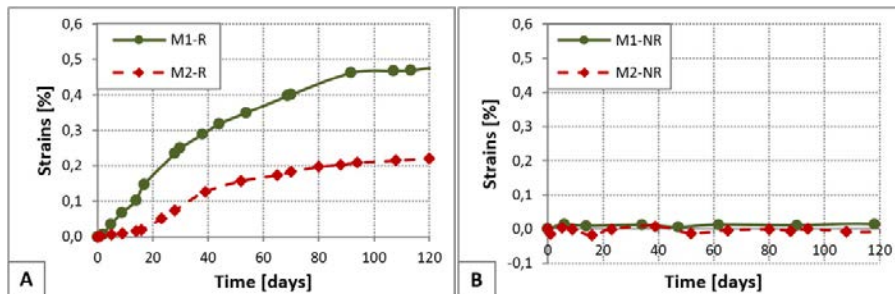

Fig. 1. Average strains of the samples stored in 1M NaOH water solution (A) or water (B).

For the samples in which the reaction took place, ASR can be calculated according to the equation [6]:

$$\Gamma_{ASR}(t) = \frac{\varepsilon_{ASR}(t)}{\varepsilon_{ASR}(t = 120 \text{ days})},\tag{1}$$

where $\varepsilon_{ASR}(t)$ is average expansion obtained after given exposure time (*t*). Average ASR extent, obtained for

series M1-R and M2-R, is presented in Figure 2. No significant expansion has been observed for series M1-NR and M2-NR. Therefore, ASR extent has not been calculated for those series.
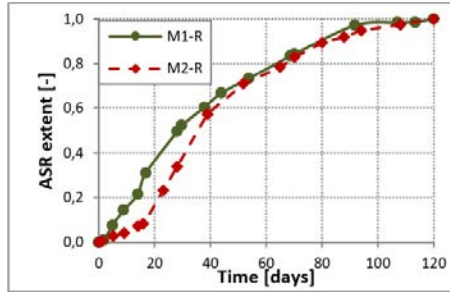

Fig. 2. Average ASR extent for mortar M1 and mortar M2 for the samples stored in 1M NaOH.

3. Mathematical model

The mathematical model is based on the mathematical formulation of the chemo-hygro-thermo-mechanical phenomena in partially saturated porous media [7, 8]. Previously the model has been applied for the alkali-silica reaction at the macroscopic scale [9]. Here the model has been further improved by taking into account diffusion of alkalis and its influence on the reaction development. Such an approach allows to analyze alkali diffusion between the material and the environment at the macroscopic scale. Furthermore, alkali diffusion from cement paste, in which the alkalis are present after cement hydration, towards the aggregate grains, inside which the reaction takes place, can be taken into account at the mesoscopic scale. It has been assumed that the aggregates are homogenous and spherical. The reaction is triggered only when threshold alkali content is reached.

Five governing equations are considered in the model: mass balance equation of dry air, mass balance equation of liquid water and water vapour, mass balance equation of alkalis, enthalpy balance equation and linear momentum balance equation. They are formulated using five state variables: gas pressure (p^g), capillary pressure (p^c), temperature (T), alkali concentration (c_{alk}) and displacement vector (**u**). It is assumed that cementitious materials is composed of solid phase (s), liquid phase (l) and gaseous phase (g). The solid phase is composed of skeleton and the ASR gel. In the liquid phase, alkalis (alk) are dissolved in the liquid water (w). The gas phase is a mixture of dry air (ga) and water vapour (gw). In the following, quantities related to the whole volume are denoted with subscripts, while values related to a given phase or its constituents with superscripts. For the sake of brevity, only final forms of the balance equations is given.

3.1. Mass balance equations

Mass balance equation of dry air can be written as:

$$\frac{n}{S_g}\frac{\overset{s}{\mathrm{D}}S_g}{\mathrm{D}t} + \frac{n}{\rho^{ga}}\frac{\overset{s}{\mathrm{D}}\rho^{ga}}{\mathrm{D}t} + \frac{1-n}{\rho^s}\frac{\overset{s}{\mathrm{D}}\rho^s}{\mathrm{D}t} + \mathrm{div}\mathbf{v}^s + \frac{1}{S_g\rho^{ga}}\mathrm{div}\left(nS_g\rho^{ga}\mathbf{v}^{gs}\right)$$
$$+ \frac{1}{S_g\rho^{ga}}\mathrm{div}\mathbf{J}_D^{ga} = \frac{\dot{m}_{alk,gel}}{\rho^s}, \tag{2}$$

where n is the porosity, S_g the pore saturation with gas, t the time, ρ^π the phase averaged density of the π-phase, $\mathbf{v}^s$ the skeleton velocity, $\mathbf{v}^{\pi s}$ the relative velocity of the π-phase with respect to the skeleton, $\mathbf{J}_D^{ga}$ the diffusive flux of

the air particles in the gas phase and $m_{alk,gel}$ the mass of alkalis bound by the gel.

Mass balance equation of water vapour may be presented in the following form:

$$\frac{n}{S_g}\frac{\overset{s}{\mathrm{D}}S_g}{Dt}+\frac{n}{\rho^{gw}}\frac{\overset{s}{\mathrm{D}}\rho^{gw}}{Dt}+\frac{1-n}{\rho^s}\frac{\overset{s}{\mathrm{D}}\rho^s}{Dt}+\mathrm{div}\mathbf{v}^s+\frac{1}{S_g\rho^{gw}}\mathrm{div}\left(nS_g\rho^{gw}\mathbf{v}^{gs}\right)$$

$$+\frac{1}{S_g\rho^{gw}}\mathrm{div}\mathbf{J}_D^{gw}=\frac{\dot{m}_{vap}}{S_g\rho^{gw}}+\frac{\dot{m}_{alk,gel}}{\rho^s},\tag{3}$$

where $\mathbf{J}_D^{gw}$ is the diffusive flux of water vapour particles in the gas phase and m_{vap} is the vapour mass related to the water evaporation.

Following form of the mass balance equation of pure liquid water can be obtained:

$$\frac{n}{S_l}\frac{\overset{s}{\mathrm{D}}S_l}{Dt}+\frac{n}{\rho^w}\frac{\overset{s}{\mathrm{D}}\rho^w}{Dt}+\frac{1-n}{\rho^s}\frac{\overset{s}{\mathrm{D}}\rho^s}{Dt}+\mathrm{div}\mathbf{v}^s+\frac{1}{S_l\rho^w}\mathrm{div}\left(nS_l\rho^w\mathbf{v}^{ls}\right)$$

$$=-\frac{\dot{m}_{vap}}{S_l\rho^w}+\frac{\dot{m}_{alk,gel}}{\rho^s},\tag{4}$$

where S_l is the pore saturation with liquid.

The mass balance equation of alkalis can be written as:

$$\frac{n}{S_l}\frac{\overset{s}{\mathrm{D}}S_l}{Dt}+\frac{n}{\rho^w}\frac{\overset{s}{\mathrm{D}}\rho^w}{Dt}+\frac{n}{c_{alk}}\frac{\overset{s}{\mathrm{D}}c_{alk}}{Dt}+\mathrm{div}\mathbf{v}^s+\frac{1}{c_{alk}S_l\rho^w}\mathrm{div}\left(c_{alk}nS_l\rho^w\mathbf{v}^{ls}\right)$$

$$+\frac{1-n}{\rho^s}\frac{\overset{s}{\mathrm{D}}\rho^s}{Dt}+\frac{1}{c_{alk}S_l\rho^w}\mathrm{div}\mathbf{J}_D^{alk}=\left(\frac{1}{\rho^s}-\frac{1}{c_{alk}S_l\rho^w}\right)\dot{m}_{alk,gel},\tag{5}$$

where c_{alk} is the alkali concentration and $\mathbf{J}_D^{alk}$ is the diffusive flux of alkali ions.

Linear momentum balance equation may be presented in the following form:

$$\mathrm{div}\mathbf{t}^{tot}+\rho\mathbf{g}=0,\tag{6}$$

where $\mathbf{t}^{tot}$ is the total stress tensor and ρ is the averaged apparent density of the medium.

Enthalpy balance equation can be written as:

$$\left(\rho C_p\right)_{eff}\frac{\overset{s}{D}T}{Dt}+\left(\rho_l C_p^l\mathbf{v}^{ls}+\rho_g C_p^g\mathbf{v}^{gs}\right)\cdot\mathrm{grad}T-\mathrm{div}\tilde{\mathbf{q}}=-\dot{m}_{vap}\Delta H_{vap}-\dot{m}_{alk,gel}\Delta H_{ASR},\tag{7}$$

where $\left(\rho C_p\right)_{eff}$ is the heat capacity of the multiphase porous medium, $\rho_l C_p^l$ of the liquid phase, $\rho_g C_p^g$ of the gas phase, $\tilde{\mathbf{q}}$ the total heat flux in the domain, ΔH_{vap} the specific enthalpy of the evaporation and ΔH_{ASR} of the alkali-silica reaction, which is assumed to be zero.

3.2. Constitutive relationships

The ASR extent is triggered in the aggregate grains after threshold alkali content, c_{lim}, has been reached. ASR extent rate is modeled as:

$$\dot{\Gamma}_{ASR} = \frac{1-\Gamma_{ASR}}{t_r}, \qquad c_{alk} \geq c_{lim}, \tag{8}$$

where t_r is characteristic time. It has been originally proposed in [6] and is calculated in the same way as in [9]:

$$t_r\left(S_l,T,\Gamma_{ASR}\right) = \tau_r\left(S_l,T\right)\frac{1+\exp\left[-\tau_L\left(S_l,T\right)/\tau_r\left(S_l,T\right)\right]}{\Gamma_{ASR}+\exp\left[-\tau_L\left(S_l,T\right)/\tau_r\left(S_l,T\right)\right]}, \tag{9}$$

Where T is temperature and $\tau_L\left(S_w,T\right)$ and $\tau_r\left(S_w,T\right)$ are constants dependent on the temperature and saturation degree according to equation:

$$\tau_r\left(S_l,T\right) = \tau_{r0}\left[\frac{E_r}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]\left(A_r S_l + B_r\right), \tag{10}$$

$$\tau_L\left(S_l,T\right) = \tau_{L0}\left[\frac{E_L}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]\left(A_L S_l + B_L\right), \tag{11}$$

where τ_{r0} and τ_{L0} are the reaction and the latency times, respectively E_r and E_L are the activation energies, A_r, B_r, A_L, B_L are the material parameters, R is the universal gas constant and T_0 is the reference temperature.

Binding of alkalis by the ASR gel is calculated according to the following equation:

$$\dot{m}_{alk,gel} = A_{alk,gel}\dot{m}_{gel,} \tag{12}$$

where $A_{alk,gel}$ is the alkali content in the gel, which can be determined experimentally, and m_{gel} is mass of the gel, calculated as in [9].

Diffusive flux of ions is given by the Fick first law:

$$\mathbf{J}_D^{alk} = -\rho^w D_{alkali}\text{grad}\left(c_{alk}\right), \tag{13}$$

where D_{alkali} is the alkali diffusion coefficient, obtained according to the following equation [9, 10, 11, 12]:

$$D_{alkali} = D_{alkali,0}e^{\alpha_T\left(T-T_{ref}\right)}S_l^{\lambda}10^{A_{\Gamma}\Gamma_{ASR}}, \tag{14}$$

where $D_{alkali,0}$ is the diffusivity of ions in reference temperature and full saturation, α_T is the temperature exponent factor, T_{ref} is the reference temperature, λ is the saturation exponent factor, and A_{Γ} is the material parameter.

3.3. Model validation

The model equations are discretized in space by means of the finite element method [13]. The time discretization is accomplished through a fully implicit finite difference scheme [13]. The obtained equation set is solved by means of a monolithic Newton-Raphson type iterative procedure using a frontal solver [7].

The model has been applied to the experimental study presented in Section 2. Since the specimens were stored either in water or 1M NaOH water solution, alkali content in which was different from the one obtained in the cement paste, alkali diffusion between the specimens and the surrounding solution should be taken into account. Alkali concentration has been analyzed in the chosen points in the mortar bars. It has been assumed that the alkali concentration in these points is characteristic also for their surroundings, as shown in Figure 3. Afterwards, alkali diffusion from cement paste into aggregate grain and ASR development have been analyzed for aggregates of different size (ag = 0.188, 0.375, 0.75, 1.5, 3 mm) and localized at different depth (dep = 1, 3, 5.5, 9, 15.5 mm) from the specimen surface. Placement of the analyzed points is presented in Figure 3. Finally, ASR extent has been calculated according to the equation:

$$\Gamma_{ASR} = \sum_{dep}\sum_{ag}\left[\eta_{ag}\eta_{dep}\Gamma_{ASR,ag,dep}(t)\right], \tag{15}$$

where η_{ag} and η_{deo} are the fractions of aggregates of given size and at different distance from the sample surface, accordingly, and $\Gamma_{ASR,ag,dep}$ is the ASR extent in a given location and for a given aggregate size. The parameters used in the simulations are summarized in Table 1.

Table 1. Parameters used in the simulations.

Parameter		M1-R	M2-R	Unit
n				
-	Aggregate	0.05	0.038	[-]
-	Cement paste	0.20	0.20	[-]
c_{lim}		0.0063	0.0110	[kg/kg]
$C_{alkali,in}$				
-	Aggregate	0.0001	0.0001	[kg/kg]
-	Cement paste	0.0092	0.0092	[kg/kg]
$D_{alkali,0}$				
-	Aggregate	$1 \cdot 10^{-14}$	$0.8 \cdot 10^{-14}$	[m^2/s]
-	Cement paste	$2.26 \cdot 10^{-11}$	$2.26 \cdot 10^{-11}$	[m^2/s]
τ_{L0}		1	1	[days]
T_{r0}		50	55	[days]
τ_{aging}		20	20	[days]
E_c		9400	9400	[J/(molK)]
E_L		4000	4000	[J/(molK)]
S_L		0.999	0.999	[-]

The alkali concentration in given points is presented in Figure 4. Comparison of the ASR extent development with the experimental results is presented in Figure 5. As can be noticed, a good accordance has been obtained.
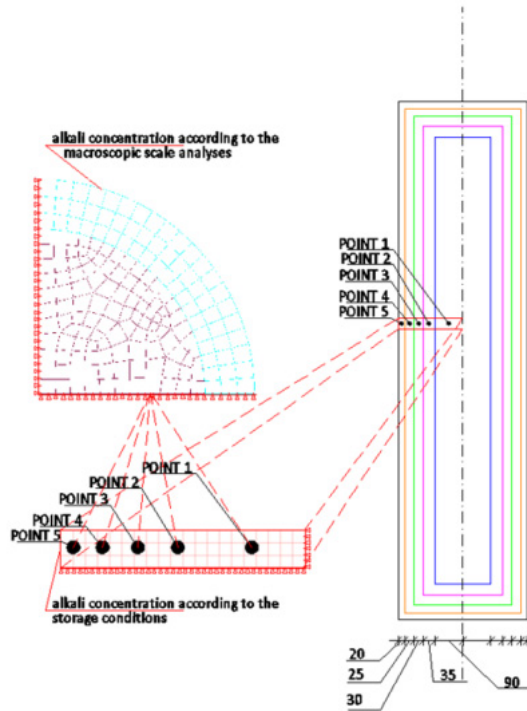
Fig. 3. Placement of the points, in which the alkali concentration has been analyzed, and areas for which it has been assumed as representative.
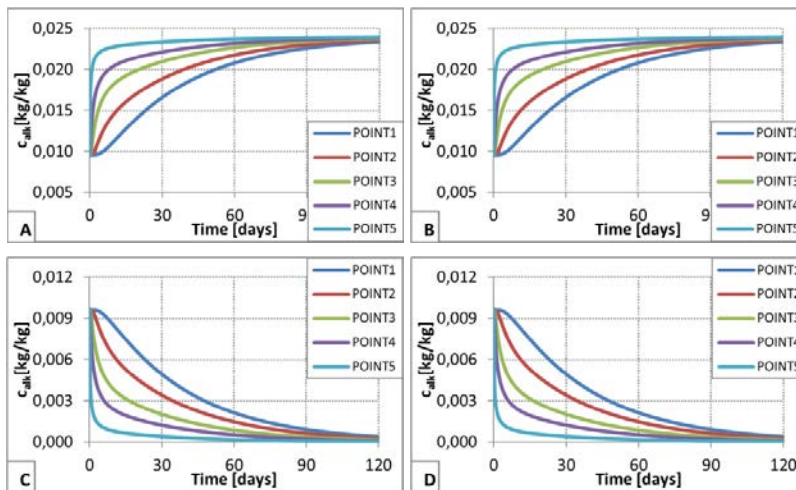

Fig. 4. Alkali concentration in given points in series M1-R (A), M2-R (B), M1-NR (C), M2-NR (D).
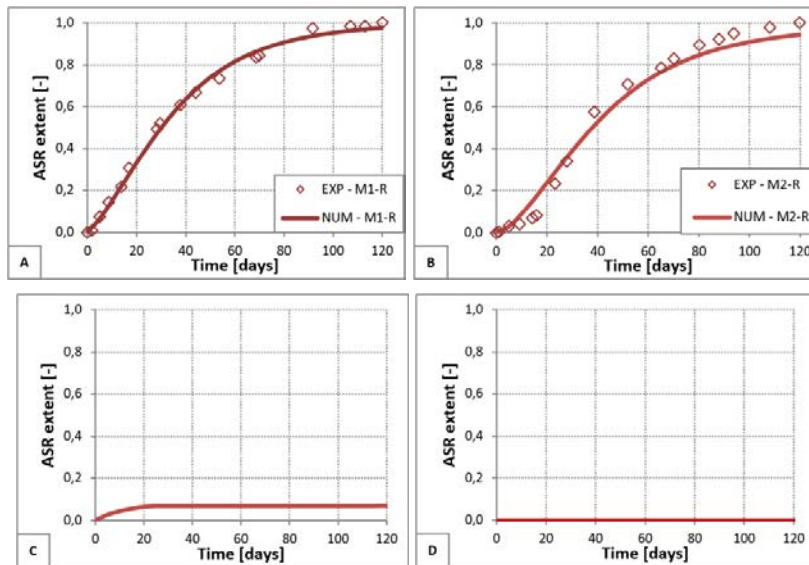
Fig. 5. ASR extent obtained for series M1-R (A), M2-R (B), M1-NR (C), M2-NR (D).

4. Conclusions

Experimental research of the ASR development has been performed. Mortar bars, prepared with two different aggregates, have been stored in 1M NaOH water solution or water. Large strains have been observed in the mortar bars stored in highly alkaline solution. Strains in the specimens stored in water have been negligible. Mathematical model of the alkali diffusion and the ASR development has been proposed within framework of the multiphase porous media. Model takes into account hygro-thermal behavior of cement-based materials. Model has been validated by comparison to the experimental data. A good accordance has been obtained. Using this approach, it is possible to take into account influence of the material microstructure on the alkali diffusion, and hence also on the reaction development. Furthermore, external alkali sources may be considered in the analyses of the ASR evolution.

References

[1] P. Rivard, M.A. Bérubé, J.-P. Ollivier, G. Ballivy, Decrease of pore solution alkalinity in concrete tested for alkali-silica reaction, Mater. Struct. 40 (2007) 42-49.

[2] S. Multon, A. Sellier, Multi-scale analysis of alkali-silica reaction (ASR): Impact of alkali leaching on scale effects affecting expansion tests, Cem. Concr. Res. 81 (2016) 122-133.

[3] T. Kim, J. Olek, H. Jeong, Alkali-silica reaction: Kinetics of chemistry of pore solution and calcium hydroxide content in cementitious materials, Cem. Concr. Res. 71 (2015), 36-45.

[4] J. Duchesne, M.A. Bérubé, Long-term effectiveness of SCM against alkali-silica reaction, Cem. Concr. Res. 31 (2001) 1057-1063.

[5] RILEM, AAR-2–Detection of potential alkali-reactivity of aggregates–The ultra-accelerated mortar bar test, Mat. Struct. 33 (2000) 283-289.

[6] F.J. Ulm, O. Coussy, L.Kefei, C.Larive, Thermo-chemo-mechanics of ASR expansion in concrete structures, J Eng Mech 126 (2000) 233-242.

[7] D. Gawin, B.A. Schrefler, Thermo-hydro-mechanical analysis of partially saturated porous materials, Eng. Comput. 13 (1996) 113-143.

[8] M. Koniorczyk, D. Gawin, Heat and moisture transport in porous building materials containing salt, J. Bldg. Phys., 31 (2008) 279-300.

[9] F. Pesavento, D. Gawin, M. Wyrzykowski, B.A. Schrefler, L. Simoni, Modeling alkali-silica reaction in non-isothermal, partially saturated cement based materials, Comput. Methods Appl. Mech. Engrg 225-228 (2012) 95-115.

[10] A. Buchwald, Determination of the ion diffusion coefficient in moisture and salt loaded masonry materials by impedance spectroscopy, Proceedings of third international Ph.D. symposium (2000) 475-482.

[11] V. Baroghel-Bouny, M. Thiéry, X. Wang, Modelling of isothermal coupled moisture-ion transport in cementitious materials, Cem. Concr. Res. 41 (2011) 828-841.

[12] E. Samson, J. Marchand, Modeling the effect of temperature on ionic transport in cementitious materials, Cem Concr Res, 37(2007) 455-468.

[13] O.C. Zienkiewicz, R.L. Taylor, The Finite Element Method. The Basis, Vol. 1, Butterworth-Heinemann, Oxford, 2000.