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A multi-species reactive transport model based on gas-ion-solid phase interaction for the carbonation of cement-based materials

Suntharalingam Sharmilan^{a,*}, Henrik Stang^b, Alexander Michel^a

^a Technical University of Denmark (DTU), Department of Environmental and Resource Engineering, 2800 Kgs. Lyngby, Denmark
 ^b Technical University of Denmark (DTU), Department of Civil and Mechanical Engineering, 2800 Kgs. Lyngby, Denmark

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ABSTRACT

This study presents a reactive transport modelling framework for understanding carbonation processes through pore solution composition, phase assemblage changes in cement-based materials, and pore solution composition changes on steel corrosion. The study emphasizes the significance of considering pore structure changes on mass transport and utilizing a surface complexation model for predicting changes in pore solution composition and comprehending its influence on steel corrosion. A clear enrichment in sodium and potassium content in carbonated regions is observed upon carbonation, which leads to a decrease in alkali concentration in the pore solution, and alkali ions are transported toward the carbonated zone. Simultaneously, the opposite behaviour is observed upon the decomposition of the solid phase. Calcium ions are transported to the carbonated zone, further increasing calcite formation near the exposed surface.

1. Introduction

In many different civil engineering applications, reinforced concrete structures are widely used. A high alkalinity pore solution with a pH value between 12.5 and 14 is formed when the solution in the pores and solid phases of the typical Portland cement reach equilibrium [1]. The high pH value in the pore solution facilitates the formation of a passive layer, which acts as a barrier and minimises the corrosion of steel reinforcement embedded in concrete [2,3]. The pH value starts to drop with the rapid dissolution of gaseous CO₂ into the alkaline pore solution during carbonation [4]. As a result of the change in the pore solution's alkaline environment, the passive layer becomes unstable [5–7], which is one of the major issues with the long-term durability of concrete structures [8–10]. In marine environmental conditions, chloride ingress co-occurs with carbonation, and their combined impact results in the severe corrosion of reinforced concrete structures [11–14]. Since concrete carbonation is critical for ensuring a long and durable service life of concrete structures, the study of the durability of concrete associated with carbonation has received much attention, especially when concrete is made with low-clinker blends [1,4,15-17].

The carbonation of cement-based material is defined as a reactive transport process in which the saturation level of pore solution in the pores reduces the diffusion of gaseous CO2 through the non-water-filled pore space. At the same time, the potential of carbon dioxide for dissolution and reaction with ionic species in the pore solution is also subject to water availability in the pores [16]. Once CO₂ enters cementbased materials at pH > 10, gaseous CO₂ starts to dissolve into the pore solution, which after that transforms into the forms of bicarbonate (HCO₃⁻) and carbonate ions (CO₃²⁻). At pH < 8, the CO₂ is directly hydrated as carbonic acid (H₂CO₃), which can then further break into two components: HCO_3^- and CO_3^{2-} . Since CO_2 dissolves into the pore solution at pH 8–10, both mechanisms are possible [4,16]. In the pore solution, calcium ions that have been re-solubilized from the solid products like Portlandite (Ca(OH)₂) react with carbonate ions to precipitate calcium carbonate [4,17–19]. Similarly, while the destabilisation of Ettringite occurs due to carbonation, other substances like gypsum, calcite, and aluminium hydroxide start precipitating [4,16]. Moreover, carbonation leads to decalcifying calcium silicate hydrate (C-S-H) [20]. The ability of the C-S-H phase to absorb alkali ions such as Na⁺ and K⁺ increases due to the Ca/Si ratio decreasing during carbonation [4,21]. As a result of carbonation, the solid phases undergo variations that also affect the pore structure and the chemical composition of the pore solution. The amount of alkali ions in the pore solution decreases due to the sorption of alkali ions by the decalcified C-S-H. Meanwhile, the free Cl content

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^{*} Corresponding author. *E-mail address:* shasu@byg.dtu.dk (S. Sharmilan).



b) Pore distribution and moisture storage

Fig. 1. a. Framework of the proposed RTM for carbonation of cement-based materials. b. The accessible pore space in the pore structure for ionic, moisture, and gas transport. c. A graphical description of mass transport due to carbonation of cement-based material. CC: calcite, CH: Portlandite, AFt: Ettringite, AFm-CO3: monocarbonate, Gp: gypsum, CSH: calcium silicate hydrate, MSHss: magnesium silicate hydrate, and SI-gel: Silica-gel.

increases as a result of the decomposition of the C-S-H phase, whereas the sulphate concentration increases upon the carbonation of Ettringite [21].

As a result of the dissolution and/or precipitation of solid phases during carbonation, the porosity and pore size distribution undergo significant changes, which has a considerable influence on mass transport [22-24]. Moreover, changes in the pore solution composition in cement-based materials may be fundamental for understanding the carbonation process and the corrosion mechanism of embedded steel in concrete structures. Therefore, studying the pore solution composition changes due to carbonation is particularly interesting for monitoring concrete structures. However, relatively few studies and information are available on pore solution composition changes upon carbonation [4,25]. Concrete is often carbonated in a dry environment, resulting in minimal free water in pores and challenging pore solution extraction [4,25,26]. Furthermore, the deterioration of concrete and understanding the governing mechanism for carbonation through accelerated experimental studies where samples are exposed to higher CO2 concentrations may be vastly different and thus difficult to interpret [27-30]. Therefore, numerical simulations can be a compelling method

to predict the deterioration of concrete structures and gain insight into the underlying phenomena driving the carbonation processes through the pore solution composition and phase assemblage changes [8,16,31–34]. In addition, numerical tools that can predict changes in cement-based materials throughout the service life can be used to select environmentally suitable binder and mix designs, reduce infrastructure costs, and estimate the lifespan of buildings that are located in different environmental conditions, such as marine environments, urban environments, etc.

Over the last few decades, several reactive transport models (RTMs) have been established to predict concrete carbonation [8,31,32,35]. Among others, RTMs have been established that combine gaseous, multi-ionic, and moisture transport models with a chemical equilibrium [31]. Simple diffusion or diffusion-advection equations are used for gaseous transport through the non-water-filled pore space. For ion mass transport in porous media, the Poisson-Nernst-Planck (PNP) equation is typically used, which is derived from a hybrid mixture theory [36,37], whereas chemical equilibrium calculations are performed through specialized tools such as PHREEQC [38-40] or GEMS [41-43]. However, current modelling approaches are limited by considering

simplified assumptions about the processes involved in the carbonation of cement-based materials, for example, mass exchange mechanisms between gas phases and pore solution during the transport calculation, diffusion of gases associated with their dissolution process with pore solution, mass flux through boundary surfaces, and the integration effect of boundary condition. Also, predictive competencies are inadequate due to the lack of fundamental relationships between phase assemblage changes, pore structure changes, and mass transport through pores. Therefore, a practical interpretation of the relations between phase assemblage, pore structure, and mass transport is also needed to consider the impact of pore structure change on mass transport due to carbonation. In addition, current RTM models without considering ion absorption on the pore surface are insufficient to predict the actual changes in the phase assemblage and composition of pore solutions due to the carbonation process and the effects of carbonation on ionic transport, for example, to analyse chloride ingress together with carbonation in concrete exposed to marine environmental conditions [44–46]. The dissolution of the C-S-H phase upon carbonation leads to the release or absorption of ions and alters the charge on the pore surface and the pore solution composition. As a result, ionic transport through the pore solution, as well as the rate of steel corrosion, will be affected by the pore solution composition. The lack of consideration of the interaction between the pore solution and the surface sites of the C-S-H phase on the pore surface in current models does not represent actual changes in pore solution composition upon carbonation, especially regarding free chloride concentration.

This study aimed to develop a reactive transport modelling framework, including multi-component gas, multi-ionic, moisture transport, and chemical equilibrium computation for understanding carbonation processes through the pore solution composition and phase assemblage changes in cement-based materials that are exposed to different boundary conditions and the effect of the composition of pore solution change on steel corrosion. To achieve this goal, the reactive transport modelling framework described in [47] is expanded to account for the carbonation of cement-based materials, including multi-component gas and ionic transport coupled with moisture transport. To accurately replicate the variations in pore solution composition and the subsequent impact of these changes on steel corrosion, a surface complexation model is employed in this study, which includes the formation of the electrical double layer and exchange interactions among the ionic solution in pores and the C-S-H surface site (=SiOH). Therefore, chemical equilibrium calculations include the equilibrium between the gas phases, aqueous species in the pore solution, hydrated solid phases, and ionic absorption on the pore surface. For interconnecting phase assemblage changes and mass transport, models for moisture conductivity, gas, and ionic diffusivity are based on the properties of pore structure and storage of liquid water in pores, taking into account the impact of the pore structure and moisture content changes on mass transport. Finally, two numerical studies were conducted. In the first numerical study, numerically predicted results were compared to experimentally measured values reported in [17] for understanding carbonation processes through the pore solution composition and phase assemblage changes in cement-based materials and the influence of pore solution composition changes on steel corrosion. In order to demonstrate the applicability of the RTM to predict the carbonation of cement-based materials prepared with a different water-to-cement ratio under various environmental conditions, the reported carbonation test results in [48] were compared to simulated results in a second numerical study.

2. Modelling approach for carbonation of cement-based materials

2.1. Outline of proposed RTM

The framework presented in [47] for an RTM in saturated cementbased material was extended to allow for analyzing the carbonation of cement-based materials by adapting additional sub-models, such as the multi-component gas and ionic transport models, which are fully coupled with moisture transport, a model to include the gas phase in chemical equilibrium calculations, a hysteresis model for determining the moisture storage in pores, a conductivity model for moisture, and a diffusivity model for multi-component gas transport. The framework for an RTM for simulating the carbonation of cement-based materials is outlined in Fig. 1a. The RTM framework is addressed in two distinct time domains: the initial stage involving cement-based materials during the curing period and the subsequent deterioration processes upon carbonation. In Fig. 1a, regions A and B represent the modelling of earlystage material development and material deterioration, respectively. Using the proposed RTM for simulating the carbonation of cement-based materials, the following parameters can be predicted: the spatial and temporal changes in the concentration and partial pressure of gaseous phase in pores, moles of dissolved gas, moisture content, vapour and liquid pressure, internal relative humidity, ionic composition in free water and the electrical double layer (EDL), and phase assemblage such as pure phases (EQ) and solid solution phases (SS) for cement-based material under carbonation. The accessible pore space in pore structure for ionic, moisture, and gaseous transport and a graphical description of mass transport due to carbonation of cement-based material are demonstrated in Fig. 1b and c, respectively. The following sections provide explanations of the ion, moisture, and gas transport, considerations of chemical equilibrium, and simulation studies conducted using the proposed RTM approach for analyzing carbonation in mortar specimens.

2.2. Governing system of equations for mass transport

2.2.1. General outline

Multi-ionic, moisture, and gas transport through a pore in unsaturated cement-based material are constructed using a one-dimensional FEM technique. For any time and spatial discretization, the ionic and gas concentration, vapour pressure, capillary pressure, relative humidity in the non-water-filled pore space, and pore solution distribution in the pore structure are simulated according to ionic, gas, and moisture transport models and applied boundary conditions. In this study, the cement-based material is assumed to be a non-deformable and rigidly porous material with constant porosity within the transport calculations. Therefore, the porosity changes are not considered during the mass transport calculation. However, at the end of each time step of chemical equilibrium calculation, the porosity changes corresponding to phase assemblage changes are implicitly taken into account in the subsequent mass transport calculation. Furthermore, pore solution and gaseous components such as vapour and CO₂(g) are expected to occupy all pores in the material under unsaturated conditions. As a result, the following relationships apply in this situation: $V_s + V_p = 1$ and $V_p = \varphi (\varepsilon_l + \varepsilon_{\nu})$ where V_s and V_p are the volume fractions of the solid and void parts in the material, respectively, φ is the total porosity, and ε_l and ε_v is the saturation of the pore solution and void in the pore, respectively.

2.2.2. Moisture transport model

Modelling of moisture transport for an unsaturated cement-based material is developed considering two-phase moisture transport, i.e., pore water and vapour, through porous media. In the present modelling approach, the governing equation for moisture transport was derived according to the total moisture mass balance of vapour and pore water in gel and capillary pores [49]. The mass balance equation of moisture transport with capillary pressure as a primary variable is given as

$$\rho_l \varphi \left(\frac{\partial \varepsilon_l}{\partial P_c} \right) \frac{\partial P_c}{\partial t} = -\nabla \left\{ \left(K_{vap}(\theta_l) + K_l(\theta_l) \right) \nabla P_c \right\} + q_l \tag{1}$$

where φ is the total porosity, ε_l the saturation of pore water, ρ_l the density of pore water $[kg/m^3]$, $K_{vap}(\theta_l)$ and $K_l(\theta_l)$ represent the con-

ductivity of vapour and pore water [kg/Pa·m·s], respectively, P_c the capillary pressure, and q_l the term used to describe water loss by hydration and differences in pore water distribution brought on by porosity changes. It is assumed that there are no hydration and pore structure changes during the transport calculation, i.e., $q_l = 0$. The vapour conductivity and liquid water conductivity proposed by Maekawa et al. [24] are adopted in the present RTM.

2.2.3. A multi-species ionic transport model coupled with moisture fluctuations

Due to the formation of the EDL in cement-based material, the diffusion of ions will follow a different path within the pore solution. Most anions and cations diffuse through free water space and the EDL, respectively [47]. For ion transport through free water (uncharged water) and the EDL (charged water) under unsaturated conditions, the previously presented set of modified Poisson-Nernst-Planck (PNP) equations in [47] are further enhanced to account for the influence of moisture fluctuation in the pores. Free water is typically present within the pore's middle region, while the electric double layer (EDL) develops on the pore's surface. Due to the no-slip condition, the velocity of liquid water near the pore surface can be neglected, and the thickness of the EDL is small compared to the typical pore diameter (see Fig. 1b). Hence, the water in the EDL is considered non-moveable water in the present approach. Therefore, the effect of liquid water flow through pores on ionic transport is considered only for ions in free water. Moreover, pores with a diameter smaller than approximately 7 nm are completely covered by an EDL [50]. Due to the formation of a fully covered EDL and the presence of high electrical potentials on the pore surface, an assumption is made that pores with a radius below a certain threshold (r_{th}) are inaccessible for multi-ionic transport [51], even if the pores are saturated (see Fig. 1b). In this study, the threshold porosity (φ_{th}) and the surface area of pores below the threshold pore radius (Ath) are calculated based on the distribution of pores and an assumed threshold pore radius. Similarly, the portion of a pore's surface (A_s) that is covered by the pore solution is computed based on the distribution of pores and the pore radius (r_c) corresponding to the point at which an interface between the pore solution and vapour phase is formed (see Fig. 1b). In free water, the governing equation for multi-ionic transport under the velocity condition is:

pore's surface that is covered by the pore solution, and t_d the thickness of the EDL, which is computed based on the Debye length [47]. Gauss's law is used to calculate the intensity of electric potential in the EDL and free water (Φ_f^T and Φ_d^T) individually. The equation for free water's acquired electric potential is,

$$\nabla \left((\varphi - \varphi_{th}) \, \varepsilon_f^l \, \zeta_0 \, \zeta_r \nabla \Phi_f^T \right) = (\varphi - \varphi_{th}) \, \varepsilon_f^l F_C \sum_{j=1}^N v^j \, C_f^{l_j} \tag{4}$$

The following equation can be used to represent the electric potential for the EDL.

$$\nabla \left(\left(A_s - A_{th} \right) t_d \zeta_0 \zeta_r \nabla \boldsymbol{\Phi}_d^T \right) = \left(A_s - A_{th} \right) t_d F_C \sum_{j=1}^N v^j C_d^{l_j}$$
(5)

where ζ_0 and ζ_r are the relative and vacuum dielectricity coefficients, respectively, and F_C the Faraday constant. In this study, the effective diffusion coefficient, $D_{i,T}^{eff}$ and effective ionic mobility, $A_{i,T}^{eff}$, introduced in [47] are used, accounting for pore structure, pore solution properties, and temperature changes.

$$D_{i,T}^{eff} = f_{\tau} \cdot f_{Tem} \cdot f_{I_s} \cdot D_{i,T_0}^{\infty} \cdot \left(1 + \frac{\partial ln\gamma_i}{\partial lnC^{l_i}}\right)$$
(6)

$$A_{i,T}^{eff} = \frac{F_C}{RT} \cdot D_{i,T}^{eff}$$
(7)

where D_{i,T_0}^{∞} is the diffusion coefficient at infinite dilution of the *i*th ion at a reference temperature (T_0), f_{τ} the tortuosity factor, and f_{Tem} and f_{I_s} correction factors for temperature and ionic strength, respectively.

2.2.4. A multi-component gas transport model coupled with moisture transport

Due to concentration gradients as well as a total gas pressure gradient, gas components can be transported through the non-waterfilled pore space (see Fig. 1b). Concentration gradients cause molecular diffusion, Knudsen diffusion, and surface diffusion of gases, whereas the differences in total pressure drive a bulk flow of the gaseous phase through unsaturated pores. In the present study, surface diffusion (since its contribution to the overall transport is hard to assess precisely) and total pressure gradient are neglected [52,53]. Moreover, due to the low density of the gaseous phase and the stable atmospheric pressure at the

$$\varphi \varepsilon_{f}^{l} \frac{\partial C_{f}^{l_{j}}}{\partial t} + \varphi C_{f}^{l_{j}} \frac{\partial \varepsilon_{l}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial ln\gamma_{j}}{\partial ln C_{j}^{l_{j}}} \right) (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla C_{f}^{l_{j}} + D^{l_{j}} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l} + A^{l_{j}} v^{j} (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla \Phi_{f}^{T} \right\} - \bar{V}^{l,s} (\varphi - \varphi_{th}) \varepsilon_{f}^{l_{j}} \nabla C_{f}^{l_{j}} - \bar{V}^{l,s} (\varphi - \varphi_{th}) C_{f}^{l_{j}} \nabla \varepsilon_{l}$$

$$\tag{2}$$

; j = 1, 2, 3..., N

where $C_f^{l_j}$ and γ_j are the mole concentrations and activity coefficient of the *j*th ion in free water, ε_f^l the saturation of free water, $\bar{V}^{l,s}$ the velocity of water with regard to the rigid porous material, v^j the valence of the *j*th ion, and D^{l_j} and A^{l_j} are the diffusion coefficient and mobility of the *j*th ion, respectively. Similarly, the governing equation for ions transport in the EDL according to the velocity condition is given by,

$$A_{s}t_{d}\frac{\partial C_{d}^{l_{j}}}{\partial t} = \nabla \left\{ D^{l_{j}} \left(1 + \frac{\partial ln\gamma_{j}}{\partial lnC_{d}^{l_{j}}} \right) (A_{s} - A_{th}) t_{d} \nabla C_{d}^{l_{j}} + A^{l_{j}} v^{j} (A_{s} - A_{th}) t_{d} C_{d}^{l_{j}} \nabla \Phi_{d}^{T} \right\}$$

$$(3)$$

$$; j = 1, 2, 3..., N$$

where $C_d^{l_j}$ is the concentration of the *j*th ion in the EDL, A_s the portion of a

boundary, the convection term is excluded from the transport equation for the gas phase. This is because the relatively lower momentum of the gas phase is insufficient to generate sufficient force for driving convection flow through the non-water-filled pore space [31]. As a result, the mass balance equation for the components of the j^{th} gas in the pore is given as follows:

$$\frac{\partial \left(\varphi\left(1-\epsilon^{t}\right)\rho_{\nu}^{g_{j}}\right)}{\partial t} + \nabla \cdot \left\{\nabla \left(D_{eff}^{g_{j}}(\theta_{l})\varphi\left(1-\epsilon^{t}\right)\rho_{\nu}^{g_{j}}\right)\right\} - q_{g-l}^{g_{j}} = 0$$

$$(8)$$

$$; j = 1, 2, 3..., M$$

where $\rho_v^{g_i}$ is the density of the j^{th} gas phase, which can be written as $\rho_v^{g_j} = M_v^{g_j} / V_v$, where $M_v^{g_j}$ and V_v are the mass and volume of j^{th} gas phase in the non-water-filled pore space, respectively, and $D_{eff}^{g_j}(\theta_l)$ the effective diffusion of the j^{th} gas constituent through the non-water-filled pore space. The first term on the left-hand side of Eq. (8) defines the gas capacity in a representative volume (REV), the gas content in the non-

water-filled pore space. Gas flux by a diffusion process is described by the first term in Eq. (8) on the right. The gas mass exchange between the gas and pore solution is indicated by the parameter $q_{g-l}^{g_j}$. It is assumed that no reaction takes place between the dissolved gaseous phase and hydrated phases during mass transport calculations. However, gas dissolution into the pore solution co-occurs with the gaseous transport through the non-water-filled pore space. Therefore, the mass transfer term between the gas phase in the non-water-filled pore space and the dissolved gas phase in the pore solution, $q_{g-l}^{g_j}$ in gas transport Eq. (8) cannot be neglected during transport calculation. In this study, the gas mass exchange term, $q_{g-l}^{g_j}$ is defined as the dissolution mass of gases in the pore solution as.

$$q_{g-l}^{g_j} = \frac{\partial \left(k_t A_{g-l} \varphi \varepsilon^l \rho_{ag}^{g_j}\right)}{\partial t}$$
(9)

where k_t and A_{g-l} are the interfacial gas transfer coefficient of the j^{th} gas constituent between the gas phase and pore solution and the contact surface area between the gas phase and pore solution, and $\rho_{ag}^{g_l}$ the density of the dissolved j^{th} gas phase in the pore solution. As the water saturation in the pores increases, the diffusion of gaseous CO₂ through the non-water-filled pore space and the contact area available to dissolve gaseous CO₂ into the pore solution decreases. To account for these mechanisms, the parameters such as $D_{eff}^{g_l}$ and A_{g-l} are adapted to limit the diffusion and dissolution of gaseous CO₂, respectively, in this gas transport model. Henry's law [54], which describes the relation between gas phase, is used to illustrate the equilibrium between the gaseous and dissolved gas phases.

$$C_{ag}^{g_j} = \frac{K_H \,\varphi_g \, P_v^{g_j}}{\gamma_g} \tag{10}$$

where C_{ag}^{g} is the molality of the *j*th gas constituent, K_H Henry's law constant, φ_g the fugacity coefficient, γ_g the activity coefficient of the *j*th gas phase in pore solution, and P_{ν}^{g} the partial pressure of the *j*th gas phase in the non-water-filled pore space. The ideal gas law of the *j*th gas phase in terms of the mass density of the *j*th gas phase in the non-water-filled pore space is,

$$P_{v}^{g_{j}} = \frac{\rho_{v}^{g_{j}} R T}{M_{g_{j}}}$$
(11)

where M_{g_j} is the mole mass of the *j*th gas phase and *R* the gas constant [J/mol·K]. By using Henry's law Eq. (10) and the ideal gas law Eq. (11), the gas mass exchange term Eq. (9) can be written in terms of the density of the *j*th gas phase in the non-water-filled pore space as,

$$q_{g-l}^{g_{j}} = \frac{\partial \left(k_{t} A_{g-l} \varphi e^{l} H_{K} \rho_{v}^{g_{j}}\right)}{\partial t}$$

$$(12)$$

where

$$H_K = \left(\frac{K_H \, \varphi_g \, R \, T}{\gamma_g}\right)$$

The mass concentration $\rho_{\nu}^{g_j}$ and the mole concentrations $C_{\nu}^{g_j}$ are related through $\rho_{\nu}^{g_j} = M_{g_j} C_{\nu}^{g_j}$. Combining Eqs. (8), (12) yield the multigas transport in the non-water-filled pore space represented in mole quantities as,

$$\varphi \left(1-\varepsilon^{l}\right) \frac{\partial C_{\nu}^{g_{j}}}{\partial t} - \varphi C_{\nu}^{g_{j}} \frac{\partial \varepsilon^{l}}{\partial t} = \nabla \left\{ D_{eff}^{g_{j}}(\theta_{l}) \varphi \left(1-\varepsilon^{l}\right) \nabla C_{\nu}^{g_{j}} - D_{eff}^{g_{j}}(\theta_{l}) \varphi C_{\nu}^{g_{j}} \nabla \varepsilon^{l} \right\} - k_{t} A_{g-l} \varphi \varepsilon^{l} H_{K} \frac{\partial C_{\nu}^{g_{j}}}{\partial t} - k_{t} A_{g-l} \varphi C_{\nu}^{g_{j}} H_{K} \frac{\partial \varepsilon^{l}}{\partial t}$$

$$(13)$$

; j = 1, 2, 3..., M

2.2.4.1. Diffusion coefficient of gas. In the case of gas transport through a narrow pore, gas molecules will frequently collide with the pore walls. Thus, Knudsen diffusion theory is applied to account for the colloidal effect of gas in the non-water-filled pore space. The effective diffusion of the *j*th gas constituent through the non-water-filled pore space, $D_{eff}^{g}(\theta_l)$ for an arbitrary temperature, *T*, is formulated as follows, accounting for the dependence of gas diffusivity on pore-structure saturation (see Fig. 1a) [24,55].

$$D_{eff}^{g_j}(\theta_l) = \frac{f_{\tau}^g \cdot D_a^{g_j}(T)}{\Omega_{\varphi}(1 - \varepsilon^l)} \int_{r_c}^{\infty} \frac{1}{1 + N_k} dV_{\nu}$$
(14)

where

$$N_k = \frac{\lambda_{j,a}}{2r}$$

where $D_{a_j}^{g_j}(T)$ is the gas diffusivity in free air space at temperature T $[m^2/s], f_{\tau}$ the tortuosity factor, Ω the three-dimensional tortuosity of a pore $(=(\pi/2)^2), N_k$ the Knudsen number, l_m the mean free path of gas molecules $[m], r_c$ the pore radius [m] at the liquid and vapour contact, and V_v the volume of vacant micro-pore space for gas transport $[m^3]$. For the binary mixture of the j^{th} gas constituent and air, the following formula is used to compute the mean free path of j^{th} gas constituent in the air $(\lambda_{j,a})$ at temperature T [56].

$$\lambda_{j,a} = \frac{k_B T}{\pi ((\sigma_j + \sigma_a)/2)^2 P_T} \frac{1}{\sqrt{1 + (M_j/M_a)}}$$
(15)

where k_B is the Boltzmann constant, P_T the total pressure, σ_j and σ_a the collision diameters for the j^{th} gas constituent and air, respectively, and M_j and M_a the molecular weights of the j^{th} gas constituent and air, respectively. By considering phase assemblage changes, the chemical equilibrium calculation determines the variations in porosity, which are subsequently employed to compute the tortuosity [57].

$$f_{\tau}^{g} = f_{\tau,0}^{g} \left[exp\left(log\left(\frac{1}{f_{\tau,0}^{g}}\right) \left(1 - \left(\frac{1}{P_{\tau}}\right)^{c}\right) \right) \right]$$
(16)

where f_r^g represents the tortuosity factor at time step t, $f_{r,0}^g$ the initial tortuosity factor, c a shape factor, and the ratio of the total porosity at time step t, φ_t , and the starting porosity, φ_0 is defined as the penalty factor, P_t . The diffusion coefficient of the j^{th} gas constituent, $D_a^{g_i}(T)$ is evaluated through the kinetic gas theory applying the Wilke and Lee method [58],

$$D_{a}^{g_{j}}(T) = \frac{\left[3.03 - \left(0.98 / M_{j,a}^{1/2}\right)\right] \cdot T^{3/2}}{P_{T} M_{j,a}^{1/2} \sigma_{j,a}^{2} \Omega_{D}} \cdot 10^{-7}$$
(17)

where

$$M_{j,a} = 2[(1/M_j) + (1/M_a)]^{-1}$$

where M_j and M_a are molecular weights of j^{th} gas constituent and air,

Table 1

Mix design of mortars, after [17,48].

Mix composition	Example 1		Example 2					
Mass [kg/m ³]	wPc50	PC55	PC60	PC65	PC70			
Cement	511.1	504.1	459.9	424.9	403.7			
Water	255.5	277.3	275.9	276.2	282.6			
Sand	1533.2	1441.8	1481.0	1508.6	1509.7			

respectively [g/mol], P_T the pressure [bar], $\sigma_{j,a}$ the characteristic length of the intermolecular force law [A°], and Ω_D the diffusion collision integral.

2.2.5. Finite element formulation

The finite element method (FEM) was used to solve the governing equations for ion, gaseous, and moisture transport under unsaturated environments. Using a weight function w for the spatial domain and a weight function W for the time domain, the governing equations Eqs. (1)–(5), (13) are separated into a spatial domain and a time domain for the finite element formulation. Utilizing Galerkin's approximation, the one-dimensional spatial scheme with linear spatial components was discretized [59,60]. The Green-Gauss theorem was applied to separate the boundary flow conditions in the mass transport. Every step implicitly solves the problem in the time domain. To prevent the staggering schemes between individual solutions of state variables, the entire connected set of equations was solved at once. A modified Newton-Raphson iteration strategy was adapted to enhance the FEM solution of the system equations while also speeding up computation [61,62].

2.3. Chemical equilibrium model

The geochemical PhreeqcRM algorithm was employed in the chemical equilibrium computation, enabling efficient parallel processing while ensuring compatibility between the transport and chemical modules. This algorithm was used to solve the mass exchange terms. q_l , $q_f^{l_j}$, $q_d^{l_j}$ and $q_{g-l}^{g_j}$ from the governing Eqs. (1)–(3), (13), accounting for the chemical interactions between gas, ions, and hydrated phases [38–40,63]. In the geochemical solver, the chemical equilibrium calculation for interactions between gas phases, aqueous species in pore solution, and hydrated solid phases, including surface absorption, is performed using the mass action laws derived from thermodynamics [47]. Here, the heterogeneous mass-action equations in terms of partial pressure and an equation for total pressure describe the equilibrium between the multi-component gas and aqueous phases [39]. Furthermore, all gas components in the gas phase are expected to be substances of ideal gas behaviour.

3. Numerical examples

Two numerical studies were conducted. The first numerical study investigated carbonation processes through the pore solution composition and phase assemblage changes in cement-based materials using experimental results for white Portland cement (wPc) under specific environmental conditions reported in [17] and the influence of the pore solution composition changes on steel corrosion. Results of the experimental study comprise the content of Portlandite and carbonate phases over time for specimens exposed to a controlled $CO_2(g)$ environmental condition and the carbonation depths as measured by phenolphthalein. In order to show the applicability of RTM to predict the carbonation of cement-based materials prepared with a different water-to-cement ratio under various environmental conditions, a second numerical study was conducted. The second numerical simulation used the reported carbonation test results for mortar specimens under various temperature and humidity conditions [47]. In the experimental studies [48], carbonation tests were conducted using a constant temperature and

Table 2

Chemical	composition	[wt%]	and	physical	characteristics	of (white)	Portland
cement (v	wPc), after [1]	7,64].					

Details	Example 1	Example 2
	wPc	PC
Chemical composition analysis [wt%]		
SiO ₂	21.81	20.23
Al ₂ O ₃	3.56	5.39
Fe ₂ O ₃	0.24	3.04
CaO	66.13	64.64
MgO	1.10	0.92
K ₂ O	0.43	0.31
Na ₂ O	0.04	0.30
SO ₃	3.37	1.91
CO ₂ (g)	0.37	1.65
CaCO ₃	3.10	3.75
Gypsum	4.10	2.44
Free lime	1.91	-
Cl	0.03	0.025
LOI 950C	2.40	2.40
Density [kg/m ³]	3080	3160
Blaine fineness [m ² /kg]	387	330

relative humidity test tank with a carbon dioxide gas concentration of 10 % to determine the effect of relative humidity and temperature on the carbonation of mortar specimens. Materials and measurements used in these two investigations are briefly summarized here, while [17,48] provide more details on preparing the mortar specimens, environmental conditions, and testing methods for numerical examples 1 and 2, respectively.

3.1. Materials

In the experimental study [17] used for the first numerical simulation, mortar samples were prepared in 40 × 40 × 160 mm³ moulds using white Portland cement (wPc, CEMI 52.5N). A water-to-cement mass ratio of 0.50 and a binder-to-sand mass ratio of 1:3 were used to prepare the wPc mortars. The mortar samples underwent a 24-hour curing process in a humid cabinet that was kept at a humidity level of 90 % and a temperature of 20 ± 1 °C. The mortar specimens were demolded and then cured in demineralized water for 91 days at 20 °C. Table 1 provides the mix design for the wPC mortar. White Portland cement (wPc), categorized in CEMI 52.5N, with a chemical composition determined in c, is shown in Table 2 for numerical example 1.

Furthermore, in the experimental study presented in [48] and adapted for the second numerical simulation, experiments were conducted, selecting different temperature and humidity levels as external environmental conditions and water-cement ratios as factors for internal material conditions. The mortar specimens were prepared using Portland cement (PC) with various water-cement ratios, namely w/c-55 % (PC55), w/c-60 % (PC60), w/c-65 % (PC65), and w/c-70 % (PC70), in $40 \times 40 \times 160 \text{ mm}^3$ moulds for carbonation tests. The mortar specimens were demolded after 24 h of air curing. After demolding, standard curing was performed for 28 days at 20 °C temperature. Before exposure to carbonation, aerial curing was performed for about ten days in a constant temperature and humidity room with a relative humidity of 50 % until mass equilibrium was nearly accomplished. Table 1 provides information about the PC mortar's mix design. For numerical example 2, the chemical composition of Portland cement (PC) classified in CEMI 52.5N was obtained from [64] and given in Table 2.

3.2. Exposure conditions

In the experimental study presented in [17], which is used as the basis for the first numerical simulation, wPc mortar specimens were kept in a controlled environment with 1 % CO₂(g) concentration (ν/ν) for 280 days at 57 ± 1 % relative humidity and 20 °C. After exposure to CO₂

Table 3

Clinker composition of the white Portland cement (wPc) and Portland cement (Pc) [wt%].

Phase composition [wt%]			Present as a solid solution in the clinker phases [wt%]			
	wPc (Example 1)	Pc (Example 2)		wPc (Example 1)	Pc (Example 2)	
Alite ^a (C ₃ S)	65.60	58.60	CaO ^e	1.97	0.00	
Belite ^a (C ₂ S)	14.90	17.20	MgO ^c	1.13	0.77	
Aluminate ^a (C ₃ A)	9.30	6.97	K ₂ O ^d	0.04	0.10	
Ferrite ^a (C ₄ AF)	0.75	9.90	Na_2O^d	0.02	0.20	
Calcite ^b	3.15	3.75	SO_3^{f}	0.99	1.19	
Bassanite ^a	0.00	2.01				
Gypsum ^c	4.54	0.43				
K ₂ SO ₄ ^d	0.74	1.66				
$Na_2SO_4^d$	0.04	0.69				

^a Determined by MAS NMR [17] and XRD [64].

 $^{\rm b}\,$ Calculated from the CO_2 content Table 2.

^c Calculated from the chemical analysis.

^d Calculated from total (Table 2) and soluble alkali content [65].

^e Calculated from the Free CaO content Table 2

^f Calculated from the distribution of sulfate [65].

Table 4

Model parameters for the numerical investigations.

Model parameters	Example 1	Example 2			
	wPc50	PC55	PC60	PC65	PC70
No of spatial elements	50	60	60	60	60
Growth factor of spatial elements	2	2	2	2	2
Total spatial distance, (mm)	15	30	30	30	30
Total exposure time, (days)	360	42	42	42	42
Time step, Δt (h)	6	6	6	6	6
Threshold pore radius, rth (nm)	2	2	2	2	2
Initial tortuosity factor, $f_{\tau,0}$	0.05	0.06	0.075	0.08	0.085
Initial gas tortuosity factor, $f_{\tau,0}^{g}$	0.05	0.06	0.075	0.08	0.085
Shape parameter, <i>c</i>	1	1	1	1	1
Interfacial gas transfer coefficient,	100	300	300	300	300
$k_{(t=293.15)}$					

for 0, 7, 14, 21, 28, 56, 91, and 280 days, carbonation depths were measured using phenolphthalein. In addition, thermo-gravimetric analysis (TGA) was used to assess Portlandite and carbonate content relative to 100 g mass of ignited mortar samples at 800 °C in the carbonated and non-carbonated areas of exposed mortars after 28 and 91 days. In the experimental study conducted in [48] and used for the second numerical simulation, the carbonation test for mortar specimens was carried out by using a constant temperature and humidity test tank with a carbon dioxide gas concentration of 10 % and promoting tests under four different temperatures, i.e., 15.0 °C, 22.5 °C, 30.0 °C, and 37.5 °C, and four different relative humidity, i.e., 35 % RH, 50 % RH, 65 % RH, and 80 % RH. After 1, 3, 7, 14, 28, 42, and 56 days of exposure, carbonation depths were measured by spraying a 1 % phenolphthalein solution on a split section of mortar specimens.

3.3. Input parameters and databases for numerical studies

In the two numerical studies, specimen size and boundary conditions are simulated according to the experiments' descriptions. In both experiments, one side of the mortar specimens was exposed to carbonation, and the other surfaces were sealed with epoxy resin. Upon carbonation, moisture loss or gain in the mortar specimens occurs through the exposed surface. However, due to the lack of pore solution continuity with the exposure environment, ionic ingress or leaching through the exposed surface does not occur in the exposed mortar specimens. Therefore, the mass transport calculations consider gaseous ingress and moisture flux (in the form of vapour phase) through the exposed surface. The hydration of the binder was computed from the degree of hydration of each clinker in the cement. For numerical examples 1 and 2, the main clinker contents, such as alite, belite, aluminates, and ferrites, were measured using MAS NMR Spectroscopy [17] and XRD-Rietveld [64], respectively. The proposed approach of Taylor [65] and chemical analyses are used to determine minor contents, which include soluble alkali sulfates (K₂SO₄ and Na₂SO₄), non-dissolved alkali oxides (K₂O and Na₂O), magnesium oxide (MgO), and gypsum. The calculated clinker content in wPC and PC cement, which are used in example 1 and example 2, respectively, is shown in Table 3.

In the numerical studies, the multi-ionic transport contained 74 ions in total and the $CO_2(g)$ gas phase in the gas transport, whereas twophase moisture, i.e., liquid and vapour, were adapted in moisture transport calculation. The reactions among gas, ions, and hydrated phases present in the cement-based material and their thermodynamic properties were defined using the CEMDATA18 database [66] (http:// www.empa.ch/cemdata) in the chemical equilibrium model. In addition, the thermodynamic data for zeolite phases that contain K and Na such as phillipsite(K), phillipsite(Na), clinoptilolite(K), clinoptilolite (Na), chabazite(K), chabazite(Na), mordenite(K), mordenite(Na) and natrolite [67-69] were adapted for the database. The CSHQss model [70,71] for the major hydrated component (C-S-H) in cement-based material was incorporated for the numerical studies. At the same time, KSiOH and NaSiOH are also included as endmembers for the C-S-H phase to enhance simulation results of the pore solution composition as well as pH value [66]. The thermodynamic database also included calcite (CC), Ettringite (AFtss), monocarbonate (CO3-AFm), Portlandite (CH), hemicarbonate (HC), hydrotalcite (Ht), and hydrogarnet (HGss). To model the carbonation of mortar specimens, other phases were included in the database, including zeolite phases, gypsum (Gp), aluminium hydroxide (Al(OH)_{mic}), silica-gel (Silica_{am}), brucite, Friedel salt, Kuzel salt, ferrihydrite-mc (FeOOH), magnesite (Mgs) and magnesium silicate hydrate (MSH_{ss}). Table A.1 summarises the reaction processes and their equilibrium constants employed in the numerical analysis. The introduced surface complexation model in [47], including the absorption reaction of the surface site (\equiv SiOH) of the C-S-H phase with ions in the pore solution and their equilibrium constants, was adapted in the numerical simulations. Table 4 provides information on the spatial and temporal discretization and the tortuosity factor for ions and gas movement, gas transfer coefficient, and other parameters for the numerical simulations. For considering accuracy and computational cost in numerical examples 1 and 2, the 15 mm and 30 mm 1D domains of mortar specimens are discretized using 50 and 60 elements with a growth factor method to create a finer mesh near the surface of the exposed boundary, respectively. Sensitivity analyses for the carbonation of mortar were used to define the time step accounting for the duration



Fig. 2. Numerical results for wPc mortar specimens after 91 days of sealed curing at 20 °C. (a) hydration of clinkers and average hydration of cement over 91 days of the curing period, (b) phase assemblage, (c) composition of the pore solution, and (d) pore size distribution.

of exposure, computational time, accumulation of charge imbalance of ions in the pore solution, and the truncation error in the exposed surface node [72].

4. Results and discussion

4.1. Numerical example 1

The simulation results for wPc mortar specimens after 91 days of sealed curing at 20 °C are presented in Fig. 2. According to the model proposed by Parrot and Killo [73] for clinker hydration, the results of the hydration model show that over 95 % of the alite and aluminate clinker is hydrated, while belite exhibits a slower reaction in wPc mortar specimens (see Fig. 2a). As shown in Fig. 2b, the simulated phase assemblage consists of C-S-H, Portlandite, Ettringite, monocarbonate, hemicarbonate, hydrogarnet, hydrotalcite, and unreacted cement. Moreover, the numerical prediction indicates that around 12 % of the volume of mortar specimens is pore space after 91 days of sealed curing, whereas nearly 31 % of the whole mortar volume comprises both hydrated and unreacted cement. Fig. 2c highlights the numerically determined composition of the pore solution of the wPc mortar specimen. Since the faster rate of alkali sulphate dissolution compared to the dissolution of the main clinkers, the composition of the pore solution in wPc mortar is dominated by alkali ions, such as Na⁺ and K⁺. Due to the solubility of major hydrated phases such as Portlandite and C-S-H, the concentration of calcium (Ca) in the pore solution is comparatively higher than that of other elements. Meanwhile, the precipitation of hydrotalcite and hydrogarnet phases decreases the concentrations of iron (Fe) and magnesium (Mg), respectively. According to the simulated results, the pH of the pore solution in the wPc mortar is approximately 13.03, which is in the reported range of pH values in [1]. Fig. 2d

illustrates the predicted cumulative pore volume and pore size distribution of wPc cement mortars after 91 days of curing at 20 °C. Numerical results indicate that nearly one-third (1/3) and two-thirds (2/3) of the total pore volumes, excluding interlayer porosity, are occupied by gel and capillary pores, respectively, whereas two threshold pore radii were observed in pore distribution. According to the distribution of the pores for non-exposed wPc mortar specimens, the peak appears to be in the range of 0.1 to 1 μ m. The threshold and peak pore radius considerably affect the ionic, gas, and moisture transport in the RTM model.

4.1.1. Moisture isotherm and transport parameters

The predicted pore distribution of wPc mortar at a depth of 0.1 mm from the exposed surface is compared in Fig. 3a before and after 360 days of exposure to 1 % CO2(g) at 20 °C and 57 % RH. The mass transport parameters, such as the moisture conductivity and the diffusion coefficient of the gas phase, primarily governing the carbonation rate of cement-based materials are directly impacted by the pore structure changes. The numerical simulation of carbonation in wPc mortar shows an increase in porosity near the exposed surface (in the fully carbonated zone), followed by a decrease within the continuous carbonation region (see Fig. 5). The simulated porosity changes demonstrate a comparable trend to that observed in other published experimental findings, e.g., [74-77]. Additionally, numerically predicted results showing the cumulative pore volume indicate that the effect is more pronounced in completely carbonated wPc mortar, where the carbonation of hydrated phases increases the capillary pore space near the exposed surface. During the carbonation process, a continuous decrease is observed in the interlayer and gel pores, which can be attributed to the decalcification of the C-S-H phase and its subsequent transformation into silica gel. The distribution of pore sizes is also predicted to move toward larger pore diameters. As a result, the peak radius



Fig. 3. Numerical results for wPc mortar samples at a depth of 0.1 mm from the exposed surface in absorption and desorption after 91 days of sealed curing at 20 °C and exposed to 1 % $CO_2(g)$ at 20 °C and 57 % RH for 360 days. (a) pore size distribution, (b) moisture isotherms, (c) $CO_2(g)$ gas diffusion, and (d) moisture conductivity.



Fig. 4. Numerical results for wPc mortar samples during carbonation (a) simulated carbonation depth compared with measured carbonation depth [17], and (b) partial pressure of CO₂(g) in pores.

in the pore distribution increases five times compared to non-exposed wPc mortar. The computed moisture isotherms based on the pore structure development of wPc mortar before and after $CO_2(g)$ gas exposure are presented in Fig. 3b. As illustrated, the computed moisture isotherms show significant differences for wPc mortar before and after carbonation. Moreover, it is shown that the water saturation level for carbonated mortar is lower than for non-carbonated mortar at particular relative humidities. The simulation results illustrate that $CO_2(g)$ exposure significantly affects moisture conductivity and gas diffusivity parameters of wPc mortar, as shown in Fig. 3c and d, respectively. The

results indicate that the carbonation of wPc mortar close to the exposed surface has increased mass transport parameters over the entire moisture range. Moreover, the carbonation of wPc mortar shows considerable effects on $CO_2(g)$ diffusivity at lower saturation levels and significant increases in moisture conductivity at higher saturation levels. A similar trend in the simulated transport parameters, including moisture conductivity and gas diffusivity, was observed in the experimental findings as reported, e.g., in [78–80].



Fig. 5. Numerical predictions of phase assemblage, carbonation depth, and pH value for wPc mortar specimens during carbonation for 28, 91, and 360 days. CZ: carbonated zone, CF: carbonation front, DF: dissolution front, and NC: non-carbonated zone.



Fig. 6. Comparison of experimental measurements [17] and numerical predictions of total Portlandite (CH), carbonate (CC), and the fraction of carbonate (CCo) formed by carbonation of phases apart from Portlandite after 28 and 91 days of carbonation. The data are given in terms of molar contents per 100 g of ignited mortars (800 °C).

4.1.2. Carbonation depth profiles

This study used experimentally measured carbonation depths in exposed wPc mortar specimens [17], using phenolphthalein pHindicator as presented in Fig. 4a, to adjust the initial tortuosity factor. A more significant deviation between simulated and measured values is found after 91 days of exposure. However, numerically simulated results are well within the error margin of the phenolphthalein measurement. Furthermore, numerically simulated results indicate a continuous reduction of carbonation rate over time, governed by the development of the $CO_2(g)$ partial pressure in the pores with depth from the exposed surface. The simulated partial pressure of $CO_2(g)$ gas inside the pores after 28, 91, and 360 days of exposure is shown in Fig. 4b. Upon carbonation of the wPc mortar specimen, the partial pressure of $CO_2(g)$ in the pores gradually increases due to its dissolution into the pore solution. Subsequently, the developed partial pressure in the pores helps transport CO_2 gas to greater depths from the exposed surface. The region of developed partial pressure in the pores is compatible with the carbonation depth and pH value drops, indicating a fully carbonated zone in cement-based material.

4.1.3. Solid phase composition of carbonated mortar

The phase changes in wPc mortar caused by carbonation were determined using the proposed modelling approach. Fig. 5 shows the results of the numerical studies, including phase assemblage, pH value,



Fig. 7. Numerical results illustrating changes in the phase content and pH profile at 1 mm depth of exposed wPc mortar.

and total porosity for wPc mortar specimens exposed to 1 % CO₂(g) at 20 °C and 57 % RH for 28, 91, and 360 days. The phase assemblage in the non-carbonated portion is shown on the right side of the figures, while the impact of carbonation on the exposed mortar specimen is presented on the left. The carbonation depth in Fig. 5 is represented by dotted lines, based on the pH value dropping below 9.7 in the pore solution. The carbonation and dissolution fronts gradually move with exposure time toward the inside of the material. In Fig. 5, the numerically predicted results show the experimentally identified zones and their progressive behaviour [9]. In the carbonated zone, calcite, silicagel, gypsum, aluminium hydroxide, ferrihydrite-mc, magnesite, magnesium silicate hydrate, and zeolite phases such as clinoptilolite(K) and mordenite(Na) mainly precipitate, while the decomposition of existing hydrated phases such as Portlandite, Ettringite, monocarbonate, hemicarbonate, C-S-H_{ss}, hydrogarnet, and hydrotalcite is observed. The numerical simulation shows that alkali binds with the decalcification of the C-S-H phase, leading to the formation of zeolite phases such as clinoptilolite(K) and mordenite(Na) during the carbonation process, which is consistent with the experimentally reported findings [4,81]. The thin layer in front of the carbonated zone is known as the carbonation front. The pH value of the pore solution subsequently decreases from approximately 13.03 to 7.83. Moreover, the simulated range of pH value drop in the pore solution upon carbonation is consistent with reported results in [4,82]. In addition, the porosity in the carbonation front decreases mainly due to the formation of Ettringite, which has a comparably higher molar volume. The dissolution front contrasts with the carbonation front, in which the decalcification of Portlandite and calcite precipitation is predicted, showing a gradual decrease in porosity.

Fig. 6a and b compare the predicted and measured contents of Portlandite and carbonate for mortar specimens after 28 and 91 days of carbonation, respectively. The total phase content of the Portlandite and carbonate is shown as moles per 100 g of ignited mortars (800 °C). Most parts of the spatial and temporal domains show high agreement between predicted and measured Portlandite and calcite content. Moreover, the experimental results validate numerical predictions on the gradual increase in carbonation depth caused by the dissolution of Portlandite and calcite precipitation. Additionally, a pH reduction occurs in the region where the amount of calcite increases and the amount of Portlandite decreases, consistent with results described in [4,17,83]. Upon carbonation, numerical results indicate a complete decomposition of the Portlandite phase in the region of carbonation depth. However, increases in calcite content were observed even after pH values dropped below 9.7, which indicates carbonation continues due to the transported CO₂ reacting with other phases, such as C-S-H, AFtss, and CO₂-AFm phases, after the complete decomposition of the Portlandite phase.

The underlying mechanisms of the carbonation process of various

phases and the development of pH are challenging to study through a single-phase assemblage presented in Fig. 5. Therefore, the dissolution of phases and calcite precipitation, including the pH profile, at 1 mm depth from the exposure surface were studied, and predicted results are presented in Fig. 7. According to the anticipated results, Portlandite is the first major hydration product to decompose and transform into calcite after around 20 days of exposure, while other hydrated phases are stable during carbonation. The results further illustrate a stable pH of approximately 13.03 during the carbonation process, identified as the dissolution front (see Fig. 7). Once all accessible Portlandite has been decomposed, the higher Ca/Si (2.25) CSHQ-JenD phase begins to decalcify down to a Ca/Si ratio of 1.33, 1.25, and 0.67, similar to the Ca/ Si ratio of the CSHQ-JenH, CSHQ-TobD, and CSHQ-TobH phase, respectively. As a result, the total C-S-H phase, except for CSHQ-JenD phase content, increases due to the decalcification of the CSHO-JenD phase up to nearly 27 days of exposure. At the same time, the decomposition of monocarbonate and the formation of Ettringite are also predicted. However, the decalcification process of CSHQ-JenD and other phase changes does not significantly alter the pH of the pore solution. After 27 days of exposure, CSHQ-JenH and CSHQ-TobD start to decompose, whereas CSHQ-TobH and AFt phases continuously increase up to 33 days of exposure. As numerical results indicate, the pH value in the pore solution starts to decrease gradually, which is shown as the first drop in Fig. 7. The second drop in pH to 9.74 is observed after nearly 33 days of exposure once almost all C-S-H except CSHQ-TobH and AFtss are decomposed by carbonation. Afterwards, mainly decalcification of the CSHQ-TobH phase continues up to 38 days of exposure at a nearly stable pH of 9.74. Finally, a third drop in pH value to 7.26 is predicted alongside the complete decomposition of the CSHQ-JenH, CSHQ-TobD, and CSHQ-TobH phase.

4.1.4. Elemental profiles

The modelling approach results, including changes in elemental composition, free water and EDL concentration, absorbed ions on the pore surface, and surface sites of the C-S-H phase for the mortar specimen after 360 days of carbonation, are given in Fig. 8. The elemental profile of the unaffected core is shown on the right side of the figures, while the carbonation impact on the mortar sample is presented on the left. As shown in Fig. 8a, the decomposition of hydrated phases and the precipitation of new solid phases lead to significant changes in the elemental profile is predicted up to a depth of approximately 0.8 cm due to $CO_2(g)$ transport in the gaseous and dissolved state. Fig. 8b illustrates an increase in the moles of dissolved $CO_2(g)$ gas through the elemental content of C in both free water and the EDL, which is consistent with the developed partial pressure of $CO_2(g)$ gas in the pores (see Fig. 8a).



Fig. 8. Profiles for wPc mortar specimens during carbonation for 360 days. a) elemental composition, which is the summation of the element included in the free pore solution, the EDL, hydrates, and surface sites, b) free water composition, c) EDL composition, d) surface absorption, and e) surface sites on the C–S–H phase.



Fig. 9. Comparison of the predicted free Na, K, S, and Cl content in the pore solution of wPc mortar (w/b-0.50) with the measured pore solution composition in the Pc mortar (w/b-0.55) [4] before and after carbonation. (UC: non-carbonated, C: carbonated). The non-shaded and shaded bars represent the predicted and measured results, respectively.



Fig. 10. Predicted chloride concentration in wPc mortar specimens before and after carbonation with (W_{EDL}) and without considering EDL formation (WO_{EDL}) . (UC: non-carbonated, C: carbonated).

Upon carbonation, a clear enrichment in both sodium and potassium content is observed as a result of the formation of zeolite phases that contain Na (mordenite(Na)) and K (clinoptilolite(K)) in the carbonated zone due to the interaction of the released absorbed sodium from the pore surface and the decalcification of the C-S-H phase (see Figs. 5 and 8d). As a result, the concentration of both sodium and potassium starts to decrease in the pore solution (see Fig. 8b and c), and subsequently. both Na and K in the pore solution of the non-carbonated zone are transported to the carbonated zone due to the concentration difference in the pore solution between the carbonated and non-carbonated zones. Thus, an increase in sodium content in the carbonated zone is observed in Fig. 8a. At the same time, the opposite behaviour is observed for both the sulphur and chloride content. The concentration of sulphur and chloride in free water increases due to the decomposition of the AFtss phase and C-S-H phase as well as the release of both absorbed sulphur and chloride from the pore surface through the decomposition of the C-S-H phase (see Figs. 6 and 8d), which results in a concentration gradient



Fig. 11. Numerical predictions of molar ratios for $[Cl^-]/[OH^-]$, $[SO_4^{2-}]/[OH^-]$, and $[CO_3^{2-}]/[HCO^{3-}]$, pH value, and carbonation depth upon carbonation of wPc mortar for 360 days of exposure. The dotted lines show the threshold value of mortar ratios for corrosion ($[Cl^-]/[OH^-] > 0.6$, $[SO_4^{2-}]/[OH^-] > 1.5$, $[CO_3^{2-}]/[HCO^{3-}] > 0.1$) [4].

(of approximately more than two orders of magnitude) in the pore solution between the carbonated and non-carbonated zone. As a result, sulphur and chloride content decrease in the carbonated zone due to the transport toward the non-carbonated zone.

The direct comparison of the predicted free Na, K, S, and Cl content in the pore solution of wPc mortar specimens (non-shaded bars) with the measured pore solution composition in the Pc (CEM1) mortar specimens by cold water extraction (CWE) before and after carbonation [4] (shaded bars) is shown in Fig. 9. For both non-carbonated and carbonated mortar, the proposed RTM framework underestimates the free Na, K, S, and Cl content compared to the measured amounts [4]. This can be attributed to a discrepancy in consideration of alkali ions as well as other ions' absorption by the surface sites of the C-S-H phase in the surface complexation model used and/or the release of some of the loosely absorbed ions from the pore surface during cold water extraction. However, a similar trend between the predicted pore solution composition in wPc mortar specimens and the measured amounts in Pc mortar specimens [4] can be observed. Upon carbonation, the numerical simulation indicates a gradual decrease in the concentration of free alkali, particularly sodium and potassium, along with an increase in sulphur and chlorine concentration.

Due to the formation of the MSH_{ss} and magnesite phases due to the

dissolution of hydrotalcite (Fig. 5), the concentration of Mg in the pore solution increased, which indicates the instability in the Mg elemental profile in the carbonated zone. In the carbonated zone, the precipitation of a calcite phase during the carbonation slightly reduces the Ca^{2+} ion concentration in the pore solution. As a result, Ca^{2+} ions in the non-carbonated zone are transported by a concentration gradient to the carbonated zone, increasing further calcite formation.

4.1.5. Free chloride concentration due to carbonation

Under marine environments, the carbonation of cement-based materials promotes chloride ingress, subsequently increasing the risk of corrosion for embedded steel reinforcement. The capability of the proposed RTM modelling framework, including the surface complexation model, was used to investigate the interaction mechanism between free chloride concentration and carbonation. The predicted free chloride concentration in the wPc mortar specimen before and after carbonation with (W_{EDL}) and without considering EDL formation (WO_{EDL}) is presented in Fig. 10. When considering the EDL formation, the predicted result shows an increase in free chloride concentration upon carbonation, consistent with the measured chloride concentration in the carbonated Pc mortar specimen [4] (see Fig. 9). However, when the EDL formation is not considered, no considerable changes in the free chloride



Fig. 12. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples prepared with different water-to-cement ratios, 50.0 % relative humidity, and 30 °C temperature (a) with (With FD), and (b) without considering a functional description of the relation between phase assemblage changes, pore structure changes, and mass transport through pores (Without FD).

[RH-80%]

 M_{WC55}

 M_{WC60}

M_{WC65} M_{WC70}

RH = 80%

T = 30°C

10

for 42 days

30

50

Relative humidity [%]

20

Time [day]

[Effect of relative humidity]

30

40

50

90

70

E_{WC55}

E_{WC60}

 $\mathsf{E}_{\mathsf{WC65}}$

E_{WC70}



Fig. 13. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples prepared with different water-to-cement ratios, 35.0 %, 50.0 %, 65.0 %, and 80.0 % relative humidity, respectively, and 30 °C temperature (a) w/c-0.55, (b) w/c-0.60, (c) w/c-0.65, (d) w/c-0.80, and (e) for 42 days of exposure.

(d)

20

15

10

0

20

15

10

5

0

Carbonation depth [mm]

0

Carbonation depth [mm]

(e)

concentration within the pore solution are observed. By incorporating the surface complexation model, the proposed modelling framework can explain the experimentally observed increase in chloride concentration. Initially, the pore surface absorbs chloride ions through the interaction between ions and surface sites of the C-S-H. Upon the carbonation, the pore surface releases the absorbed chloride ions as a consequence of the decomposition of the C-S-H phase. As a result, a free chloride concentration increase in the pore solution is observed during carbonation. Hence, for a more accurate prediction of the changes in free chloride concentration in the pore solution (and, ultimately, initiation of reinforcement corrosion), incorporating the interaction between the pore solution and pore surface is crucial in the RTM modelling framework.

4.1.6. Effect of composition of pore solution on corrosion due to carbonation

Upon carbonation of cement-based material, several factors can influence the corrosion of steel reinforcement. Among these, the composition of the pore solution is of utmost importance for understanding the



Fig. 14. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples prepared with different water-to-cement ratios, 50.0 % relative humidity, and 15 °C temperature (a) without (Without TE), and (b) with accounting temperature effect on the interfacial gas transfer coefficient (With TE).

corrosion process of embedded steel reinforcement in concrete. Upon carbonation of wPc mortar for 360 days of exposure, Fig. 11 illustrates the simulated changes in molar ratios of [Cl⁻]/[OH⁻], [SO₄²⁻]/[OH⁻], and $[CO_3^{2-}]/[HCO^{3-}]$ with (W_{EDL}) and without considering EDL formation (WO_{EDL}), as well as pH value and carbonation depth. Increases in the corrosion rate of steel reinforcement [84] may be observed for concentrations of chlorides and sulfates higher in relation to the hydroxyl concentration [85,86] and carbonate concentrations lower than bicarbonate in the pore solution. In the pore solution of non-carbonated mortar, the molar ratios of $[Cl^-]/[OH^-]$ and $[SO_4^{2-}]/[OH^-]$ are below the corrosion threshold levels. However, the pore solution mainly contains carbonates, leading to an exceptionally high $[CO_3^{2-}]/[HCO^{3-}]$ ratio. When EDL formation is taken into consideration during the carbonation of mortar, the simulation results indicate that the molar ratios of [Cl⁻]/[OH⁻] and [SO₄²⁻]/[OH⁻] start to increase above the threshold values of 0.6 and 1.5, respectively, while $[CO_3^{2-}]/[HCO^{3-}]$ decreases below the threshold value of 0.1. Consequently, these changes are anticipated to accelerate the corrosion of reinforcement. In addition, the region where the molar ratio changes upon carbonation of mortar are consistent with the carbonation depth, and the pH value drops. When the formation of the EDL is not taken into account, the molar ratios of [Cl⁻]/[OH⁻] in both carbonated and non-carbonated regions are above the threshold value of 0.6. However, changes in the molar ratios of [SO₄²⁻]/[OH⁻] and [CO₃²⁻]/[HCO³⁻] show a somewhat similar trend as observed in the predicted results when considering the EDL formation. The predicted variations in the pore solution highlight the significance of incorporating surface complexation into the RTM modelling framework for investigating the corrosion of steel reinforcement, particularly based on the molar ratios of [Cl⁻]/[OH⁻].

4.2. Numerical example 2

4.2.1. Applicability of RTM under various relative humidity conditions

In this study, the simulated carbonation depth using the proposed RTM framework, achieved by adjusting the initial tortuosity factor (see Table 4) based on experimentally measured carbonation depth of PC mortar samples prepared with different water-to-cement ratios at 50.0 % relative humidity and 30 °C temperature [48], while considering a functional description (With FD) of the relationship between phase assemblage changes, pore structure changes, and mass transport through pores, is presented in Fig. 12a. To demonstrate the importance of the functional description in the modelling framework, the simulated carbonation depth without considering it (Without FD) for the adjusted initial tortuosity factor mentioned above is presented in Fig. 12b.

Without considering a functional description, the simulated result indicates an underestimate of carbonation in exposed Pc mortar specimens. Upon carbonation, the variation in pore distribution close to the exposure surface, as well as increases in porosity due to phase assemblage changes, were observed in simulated results. Therefore, gas mass transport through the non-water-filled pore space increases upon carbonation, further accelerating the carbonation process in the Pc mortar specimen. Therefore, when accounting for pore structure changes on mass transport through pores using the proposed functional description, an increase in the carbonation rate for all specimens was observed in Fig. 12b. Furthermore, using an adjusted initial tortuosity factor for carbonation depth in mortar samples at 50.0 % relative humidity and 30 °C temperature, the proposed functional description for accounting for pore structure changes in mass transport through pores was examined under various relative humidity conditions. Fig. 13 compares simulated and measured carbonation depth of PC mortar samples prepared with different water-to-cement ratios, 35.0 %, 50.0 %, 65.0 %, and 80.0 % relative humidity, respectively, and 30 °C temperature. A good agreement between simulated and experimentally measured values is observed for the carbonation depth of mortar specimens exposed to different relative humidity, which indicates that the proposed model, including a functional description of the relation between phase assemblage changes, pore structure changes, and mass transport through pores, can be utilized to predict the carbonation process of cement-based material exposed to various ranges of relative humidity. As illustrated in Fig. 13, mortar specimens with a higher water-to-cement ratio show higher carbonation for all relative humidity levels. Numerical results indicate that changes in relative humidity around mortar specimens have a more significant effect on carbonation depth and further suggest that very low as well as high relative humidity levels slow down the carbonation rate in cement-based material. Moreover, mortar specimens exposed to 50 % relative humidity show the most considerable carbonation depth compared with other exposure conditions (see Fig. 13e). The carbonation depth of mortar specimens exposed to 80 % relative humidity is significantly lower than in exposure conditions with lower relative humidity. The simulation outcome demonstrates that when a mortar specimen is exposed to higher relative humidity, such as 80 % or more, the moisture storage inside the pores of the mortar increases significantly compared to exposure to lower relative humidity (see Fig. 3b). As a result of limited space for gas mass transport, carbonation depth in mortar specimens exposed to 80 % relative humidity considerably decreases at a higher saturation level of moisture.





Fig. 15. Comparison between simulated and measured carbonation depth [48] of Pc mortar samples with different water-to-cement ratios exposed to 15.0 °C, 22.5 °C, 30.0 °C, and 37.5 °C, respectively, and 50 % relative humidity. (a) w/c-0.55, (b) w/c-0.60, (c) w/c-0.65, (d) w/c-0.80, and (e) for 42 days of exposure.

4.2.2. Applicability of RTM under various temperature conditions

Using an adjusted initial tortuosity factor (see Section 4.2.1), simulated results without considering the temperature effect on the interfacial gas transfer coefficient (Without TE), along with the experimentally measured carbonation depth of PC mortar samples prepared with different water-to-cement ratios at 50.0 % relative humidity and 15 °C temperature [48], are presented in Fig. 14a. Simulated results, disregarding the temperature effect on the interfacial gas transfer coefficient, indicate an overestimate of carbonation in exposed PC mortar

specimens. The increase in temperature accelerates both the dissolution of gas into a pore solution and the diffusion coefficient of the gas phase. Nevertheless, based on the mass balance equation for gas transport, increased gas dissolution into the pore solution reduces the quantity of gas phase transport through the non-water-filled pore space. By reducing the moles of gas transport through the air void space, a decrease in the carbonation rate can be anticipated in cement-based materials. Therefore, it was decided that the effect of temperature on the dissolution of the gas phase into the pore solution can be considered by adjusting the interfacial gas transfer coefficient. By comparing simulated and measured carbonation depth under various temperatures, a relation for the interfacial gas transfer coefficient accounting for temperature is proposed as

$$k_{t} = k_{(t=293.15)} \cdot exp\left(\frac{E_{0}}{RT_{0}} - \frac{E_{0}}{RT}\right)$$
(18)

where $k_{(t=293,15)}$ is the interfacial gas transfer coefficient of the j^{th} gas constituent between the gas phase and pore solution at a reference temperature (t = 293.15 K), E_0 the reference activation energy for gas dissolution ($E_0 = 25220 \text{ J/mol}$), R the universal gas constant, T_0 the reference temperature ($T_0 = 293.15$ K), and T the absolute temperature (K). After incorporating the effect of temperature on gas dissolution (With TE), an improvement in the predictability of the proposed RTM was observed compared to the simulated results that did not account for the effect of temperature on gas dissolution, as shown in Fig. 14b. Furthermore, the proposed function for accounting for the effect of temperature on gas dissolution was examined for various PC mortar specimens prepared with different water-to-cement ratios under various temperature conditions. Fig. 15 shows a comparison between simulated and measured carbonation depths for PC mortar samples prepared with different water-to-cement ratios exposed to 15.0 °C, 22.5 °C, 30.0 °C and 37.5 °C, and 50 % of relative humidity. The simulated carbonation depth incorporating the proposed temperature effect on gas dissolution agrees well with experimentally measured values for mortar specimens exposed to various temperatures. The results show that the specimens for each water-cement ratio exhibit a steady increase in the carbonation depth with temperature increases.

5. Conclusions

For understanding carbonation processes through the pore solution composition and phase assemblage changes in cement-based materials and the influence of pore solution composition changes on steel corrosion, the reactive transport modelling framework presented in [47] was extended, including multi-component gas, multi-ionic, and moisture transport coupled with a chemical equilibrium computation. Using Henry's law, the multi-component gas transport model was developed, including gas dissolution into the pore solution. A modelling approach for moisture conductivity and gas and ionic diffusivity based on the pore structure and moisture storage was presented to account for pore structure changes on mass transport.

By adjusting the initial tortuosity factor based on carbonation depth, the results of the first numerical study demonstrate good agreements in both spatial and temporal domains between the measured and numerically predicted content of Portlandite and carbonate. The zones related to the carbonation process, such as the carbonated zone, carbonation front, dissolution front, and non-carbonated zone, were clearly identified in the numerical simulation. Initially, the Portlandite phase was decomposed upon carbonation, whereas other hydrated phases were stable. After the complete decomposition of the Portlandite phase, the C-S-H phase with a higher Ca/Si ratio (CSHQ-JenD) starts to decalcify, and subsequently, the lower Ca/Si C-S-H phases and AFt form. Simultaneously, the decomposition of monocarbonate is also predicted. Finally, all C-S-H phases and AFt were completely decomposed. During this carbonation process, three drops in the pH value were observed.

The significance of employing a surface complexation model is emphasized in this study to predict the actual changes in the composition of the pore solution and evaluate the implications of these changes on steel corrosion. The simulation results show that changes in the phase assemblage accompany changes in the composition of the pore solution. A fundamental understanding of the carbonation process, particularly related pore solution changes, is indispensable to elucidating the mechanisms of steel corrosion in reinforced concrete. A clear enrichment in sodium and potassium content in carbonated regions is observed upon carbonation. As a result, the concentration of both sodium and potassium starts to decrease in the pore solution, and alkali ions are transported toward the carbonated zone. At the same time, the opposite behaviour is observed for both the sulphur and chloride content. The increase in the concentration of sulphur and chloride in the pore water was observed due to the dissolution of the solid phases. Calcium ions are transported to the carbonated zone, further increasing calcite formation near the exposed surface. Upon carbonation of wPc mortar, the molar ratios of [Cl⁻]/[OH⁻] and [SO₄²⁻]/[OH⁻] in the pore solution start to increase above the threshold values of 0.6 and 1.5, respectively, while $[CO_3^{2-}]/[HCO^{3-}]$ falls below the threshold value of 0.1 as the bicarbonate concentration increases. It indicates that pore solution composition changes upon carbonation promote reinforcement corrosion. In addition, the region where the molar ratio changes upon carbonation of mortar is consistent with the carbonation depth, and the pH value drops.

In the second numerical study, the applicability of the proposed RTM was examined across various conditions of temperature and relative humidity. Within the framework of the RTM, the importance of accounting for changes in pore structure on mass transport upon carbonation is demonstrated by comparing the simulated carbonation depth with the measured value for mortar specimens exposed to various relative humidity conditions. Numerical results indicate that mortar specimens exposed to high or low relative humidity exhibit lower carbonation depths. On the other hand, the highest carbonation rate occurs at a relative humidity range between 40 % and 60 %. Furthermore, a relation for the interfacial gas transfer coefficient was proposed to account for the impact of temperature on gas dissolution into pore solution. Numerical results highlighted that an increase in temperature results in a steady increase in the carbonation depth of the mortar specimens.

CRediT authorship contribution statement

Suntharalingam Sharmilan: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Henrik Stang:** Validation, Resources, Supervision, Project administration, Funding acquisition. **Alexander Michel:** Validation, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Thermodynamic database

Table A.1 presents the dissolution reaction of phases and associated thermodynamical information based on the CEMDATA18 database [66].

Table A.1

Thermodynamic properties of the phases at 25 °C in the chemical equilibrium model.

Details of phase		Reaction equation	log K
Pure phases	Notation		
Calcite	Calcite	$CaCO_3 \Rightarrow CO_3^{2-} + Ca^{+2}$	-8.480
Hemicarbonate	HC	$(CaO)3Al_2O_3(CaCO_3)0.5(CaO_2H_2)0.5(H_2O)11.5 + 5H^+ \\ \doteqdot 0.5CO_3^{-2} + 4Ca^{+2} + 2AlO_2^- + 14.5H_2O(2A_2+14) + 2AlO_2^- $	40.870
Hydrotalcite	Ht	$Mg_4Al_2O_7(H_2O)10 + 6H^+ = 4Mg^{2+} + 2AlO_2^- + 13H_2O$	27.981
Monocarbonate	CO ₂ -AFm	$\rm Ca_4Al_2CO_9(H_2O)11 + 4H^+ {\Leftarrow} \rm CO_3^{2-} + 4Ca^{2+} + 2AlO_2^- + 13H_2O$	24.530
Portlandite	CH	$Ca(OH)_2 + 2H^+ \Rightarrow Ca^{2+} + 2H_2O$	22.800
AlOHmic	Al(OH) _{mic}	$Al(OH)_3 = AlO_2^- + H^+ + H_2O$	-14.670
Silica gel	Silica gel	$SiO_2(H_2O)2 \rightleftharpoons SiO_2 + 2H_2O$	-3.018
Ferrihydrite-mc	FeOOHmic	$\text{FeOOH} \Rightarrow \text{FeO}_2^- + \text{H}^+$	-19.600
Brucite	Brucite	$Mg(OH)_2 + 2H^+ \rightleftharpoons Mg^{2+} + 2H_2O$	16.840
Friedel salt	Friedel salt	$Ca_{4}Al_{2}Cl_{2}(OH)12(H_{2}O)4 + 4H^{+} \rightleftharpoons 2Cl^{-} + 4Ca^{2+} + 2AlO_{2}^{-} + 12H_{2}O$	-2.714
Kuzel salt	Kuzel salt	$Ca_{4}Al_{2}Cl(SO_{4})0.5(OH)12(H_{2}O)6 + 4H^{+} \rightleftharpoons Cl^{-} + 4Ca^{2+} + 0.5SO_{4}^{2+} + 2AlO_{2}^{-} + 14H_{2}O(A) + 2AlO_{2}^{-} + 2AlO_$	-19.600
Gypsum	Gypsum	$CaSO_4(H_2O)2{\Rightarrow}Ca^{2+}+SO_4^{2+}+2H_2O$	-4.581
Magnesite	Mgs	$MgCO_3 = \mathrm{CO}_3^{-2} + \mathrm{Mg}^{+2}$	-8.288
Natrolite	NAT	$Na_{2}(Al_{2}Si_{3})O10(H_{2}O)2{\Leftarrow}2AlO_{2}^{-}+2Na^{+}+3SiO_{2}+2H_{2}O$	-26.600
Phillipsite(K)	PHI(K)	$K_{2.5}(Al_{2.5}Si_{5.5}O_{16})(H_2O)5{\Rightarrow}2.5AlO_2^-+2.5K^++5.5SiO_2+5H_2O$	-42.600
Phillipsite(Na)	PHI(Na)	$Na_{2.5}(Al_{2.5}Si_{5.5}O_{16})(H_2O)5{=}2.5AlO_2^- + 2.5Na^+ + 5.5SiO_2 + 5H_2O$	-39.375
Clinoptilolite(K)	CLI(K)	$K_{1.01}(Al_{1.01}Si_{4.99}O_{12})(H_2O)2.3{\Leftarrow}1.01AlO_2^- + 1.01K^+ + 4.99SiO_2 + 2.3H_2O$	-26.800
Chabazite(K)	CHA(K)	$K_2(Al_2Si_4O_{12})(H_2O)4=2AlO_2^- + 2K^+ + 4SiO_2 + 4H_2O$	-32.300
Chabazite(K)	CHA(Na)	$Na_{2}(Al_{2}Si_{4}O_{12})(H_{2}O)6{\Rightarrow}2AlO_{2}^{-}+2Na^{+}+4SiO_{2}+6H_{2}O$	-31.900
Mordenite(K)	MOR(K)	$K_{0.65}(Al_{0.65}Si_{5.35}O_{12})(H_2O)2.3{\Leftarrow}0.65AlO_2^- + 0.65K^+ + 5.35SiO_2 + 2.3H_2O_2 + 2.3H_2$	-22.000
Mordenite(Na)	MOR(Na)	$Na_{0.72}(Al_{0.72}Si_{5.28})O12(H_2O)2.71{\Rightarrow}0.72AlO_2^-+0.72Na^++5.28SiO_2+2.71H_2O$	-22.500

Details of phase		Reaction equation	log K	
Solid solutions	End member			
AFtss	SO4-AFt	$(({\rm H_2O})_2)Ca_6Al_2({\rm SO}_4)3({\rm OH})12({\rm H_2O})24 + 4{\rm H^+} \rightleftharpoons 6Ca^{2+} + 3{\rm SO}_4^{2-} + 2{\rm AlO}_2^- + 34{\rm H_2O}$	11.100	
	SO4-AFt{30}	$Ca_{6}Al_{2}(SO_{4})3(OH)12(H_{2}O)24 + 4H^{+} = 6Ca^{2+} + 3SO_{4}^{2-} + 2AlO_{2}^{-} + 32H_{2}O$	11.702	
HGss	Si0.84-(Al)HG	$(AIFeO_3)(Ca_3O_3(SiO_2)0.84(H_2O)4.32) + 4H^+ \leftrightarrows FeO_2^- + 3Ca^{+2} + AIO_2^- + 6.32H_2O + 0.84SiO_2 + 6.34H_2O + 0.84SiO_2 + 6.32H_2O + 0.84SiO_2 + 6.34H_2O + 0.84SiO_2 + 6.34H_2O + 0.84F_2O + 0.85F_2O + 0.84F_2$	22.280	
	Si0.84-(Fe)HG	$(FeFeO_3)(Ca_3O_3(SiO_2)0.84(H_2O)4.32) + 4H^+ \rightleftharpoons 2FeO_2^- + 3Ca^{2+} + 6.32H_2O + 0.84SiO_2$	19.981	
CSHQss	CSHQ-TobH	$(CaO)0.6667(SiO_2)1(H_2O)1.5 + 1.3334H^+ \leftrightarrows 0.6667Ca^{2+} + 2.1667H_2O + SiO_2O^{2+} + 2.1667H_2O^{2+} + 2.167H_2O^{2+} + 2.167H_2O^{2+} + 2.1667H$	8.287	
	CSHQ-TobD	$((CaO)1.25(SiO_2)1(H_2O)2.75)0.6667 + 1.66675H^+ \rightleftharpoons 0.833375Ca^{2+} + 2.6668H_2O + 0.6667SiO_2 + 0.$	13.655	
	CSHQ-JenH	$(\text{CaO})1.3333(\text{SiO}_2)1(\text{H}_2\text{O})2.1667 + 2.6666\text{H}^+ \leftrightarrows 1.3333\text{Ca}^{2+} + 3.5\text{H}_2\text{O} + \text{SiO}_2$	22.179	
	CSHQ-JenD	$(CaO)1.5(SiO_2)0.6667(H_2O)2.5 + 3H^+ \rightleftharpoons 1.5Ca^{2+} + 4H_2O + 0.6667SiO_2$	28.730	
	NaSiOH	$((\text{NaOH})2.5\text{SiO}_2\text{H}_2\text{O})0.2 + 0.5\text{H}^+ {\rightleftharpoons} 0.5\text{Na}^+ + 0.7\text{H}_2\text{O} + 0.2\text{SiO}_2$	5.649	
	KSiOH	$(({\rm KOH})2.5{\rm SiO_2H_2O})0.2 + 0.5{\rm H^+}{\rightleftharpoons}0.5{\rm K^+} + 0.7{\rm H_2O} + 0.2{\rm SiO_2}$	5.764	
MSHss	M075SH	$Mg1.5Si_{2}O5.5(H_{2}O)2.5{\Leftarrow}1.5Mg^{2+} + 2SiO_{2} + 3OH^{-} + H_{2}O$	-28.800	
	M15SH	$Mg1.5SiO3.5(H_{2}O)2.5{\leftrightarrows}1.5Mg^{2+} + 1SiO_{2} + 3OH^{-} + H_{2}O$	-23.570	

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