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A model for the calculation of combined chemical reactions and transport processes and its application to the corrosion of mineral-building materials

Part I. Simulation model

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Abstract

The numerical simulation of corrosion processes can be a valuable tool for the planning of durable structures exposed to chemical attack and for planning of their maintenance and repair. In this paper, a simulation model—incremental in time and space—of corrosion of mineral-building materials is described. The model combines the calculation of transport processes with the quantitative simulation of chemical reactions. The following transport processes are incorporated: capillary suction, diffusion of solved species (including the influence of the diffusion potential), water vapor diffusion, and diffusion of solved species through the inner surface of cracks. The reactions are simulated by the repeated calculation of the thermodynamic and kinetic stable phase assemblage. Due to the thermodynamic module, the simulation does not depend on the specific reaction. Additional modules are incorporated for the actualization of transport parameters and material strength as well as for the expansion in the case of sulphate attack.

Keywords: Kinetics; Thermodynamic calculations; Durability; Transport properties; Modeling

The research on the corrosive deterioration of mineral-building materials is characterized by a phenomenological style of investigation. The prediction of the corrosion resistance by the exposition of specimens to aggressive substances is extremely time-consuming. The potential of accelerating such experiments is restricted. Each change of the material properties or of the properties of the corrosive substance imply the need for new experimental investigations. The prediction of mineral-building material corrosion as a function of time and place is only possible in some special cases (e.g., carbonation). Hence, it is promising to mathematically simulate such processes. The simulation of corrosion can be a valuable tool for the planning of the durability of buildings (e.g., concrete structures subjected to chemical attack) and of maintenance and repair concepts. In this paper, we describe a computer model for the simulation of mineral-building material corrosion. A corrosion process consists of various partial processes: transport processes, time dependent chemical reactions, and several corrosive or noncorrosive effects caused by the changes of the phase assemblage: strength loss, loss of mass, expansion, cracking, and changes of the transport parameters. We started the research work with the concept of calculating each of the partial processes by a suitable algorithm and linking them together in a calculation that is incremental in time and space. The structure of the computer program is shown in Fig. 1.

The simulation model consists of a preprocessor (preparation of onset data, e.g. the dimensions of the volume elements), a postprocessor, and the main batch program. Only the main program is described here. The model was verified by experiments concerning the corrosion of cement mortar by sulphate solutions and acid, the corrosion of cement mortar and concrete in a sewage purification plant (ammonium attack), and the corrosion of a sandstone with calcitic binder by acidic solutions with and without sulphate content. The results of the experiments and of the corresponding calculations will be discussed in the second part of this paper. A list of onset data, determined experimentally or drawn from the literature, will be presented also. For more information on the model and experimental work, we refer to a previously published work [1].

1. Simulation of the chemical reactions

The chemical reactions are simulated by the iterative calculation of the phase assemblage in each volume element

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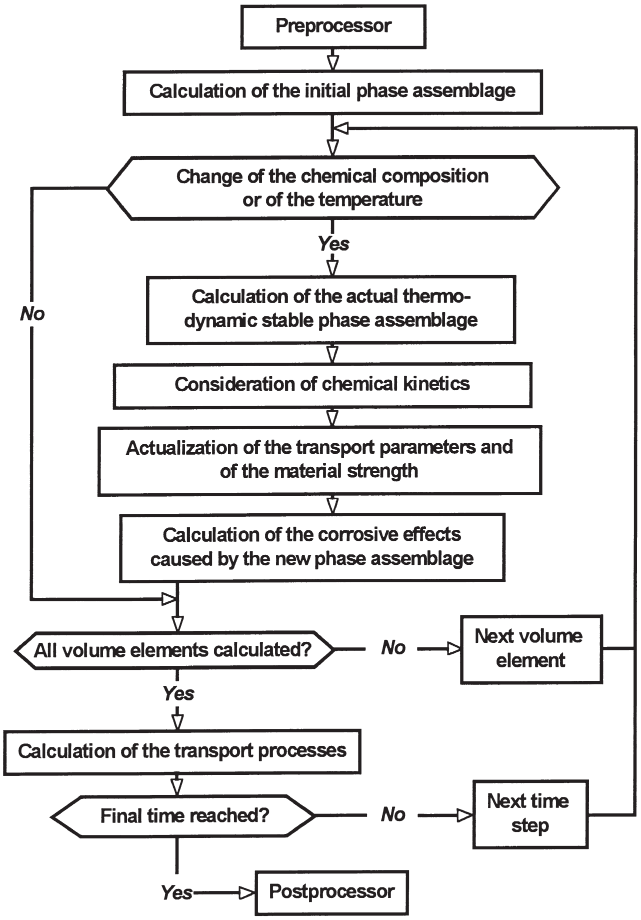

Fig. 1. Structure of the simulation algorithm.

and at each time step. This module comprises two algorithms: a calculation of the phase assemblage at thermodynamic equilibrium linked with a calculation of the chemical kinetics of the reactions.

1.1. Thermodynamic stable phase assemblage

This algorithm is the basis for using the model for the simulation of very different kinds of corrosion processes. The algorithm identifies and calculates the proceeding reactions without assistance of the operator. It is also possible to simulate the chemical attack by solutions containing many different kinds of corrosive and noncorrosive substances.

For the calculation of the thermodynamic stable phase assemblage, we use the algorithm of Storey and Van Zeggeren [2–4], which was improved in some respects. It is an optimization algorithm (minimization of the Gibbs energy of the system) that approaches the thermodynamic equilibrium iteratively. This method is very suitable because of its numerical stability. This is important, because the algorithm has to be repeated some ten thousand times during one simulation. Furthermore, there is normally no need for chemical reaction equations. The only information required are the stoichiometric coefficients of the concerned chemical species and their thermodynamic data. Finally, the calculation can be started from every phase assemblage that nearly fulfills the condition of mass balance. There is no need for an approximate solution.

Important properties for the calculation of chemical equilibrium are the chemical potential and the Gibbs energy of the species. Their calculation as a function of the temperature, the hydrostatic pressure, and the composition of the existing solutions can be drawn from several thermodynamic textbooks (e.g., [1,5,6]). The required thermodynamic data were mostly drawn from Babushkin et al. [7] and Taylor [8]. Some critical comments on these data are given in previous work [1] and will be discussed in the second part of this paper.

The algorithm is able to calculate the phase assemblage of systems containing solids, liquids, solved, and gaseous species. The ability to calculate the chemical composition of the material pore solution is an important requirement for the calculation of the transport processes of the solved ions. The activity coefficients of solved ions, solved neutral species and the solvent are calculated by the help of the Pitzer-theory and the Gibbs-Duhem equation [9,10] (for data see: [9,11,12]). The solid phases can at present only be treated as ideal solutions. Only ideal gases can be treated. The applied algorithm is about five times faster than that of Storey and Van Zeggeren because it is possible to choose a greater step-size parameter. The algorithm works as follows (for detailed information see [1]). The notations were chosen according to previous works [2,3].

1. At the beginning of the thermodynamic calculation the initial elemental abundance N_j of the chemical element j is calculated. N_j must not be changed by the thermodynamic module. See Eq. (1).

$$N_j = \sum_{i=1}^{N} \alpha_{ji} \cdot n_i \quad (j = 1,2, \ldots M) \tag{1}$$

   where α_{ji} is the number of atoms of the chemical element j in one formula unit of species i; n_i is the number of moles of the species i; N is the number of species in the system; M is the number of chemical elements in the system.
2. The function of the steps 2–7 is to shift the set of n_i in the direction of the thermodynamic equilibrium. First it is necessary to calculate the chemical potentials of the species *i*.
3. Calculation of the Gibbs energy of the system.
4. The system to solve for the Lagrangian multipliers Θ_j is shown in Eq. (2).

$$\sum_{j=1}^{M} \left(\sum_{i=1}^{N} \alpha_{ki} \cdot \alpha_{ji} \cdot {n'_i}^2 \right) \cdot \Theta_j = \sum_{i=1}^{N} \alpha_{ki} \cdot \mu'_i \cdot {n'_i}^2$$

$$(k = 1, 2, \ldots M) \tag{2}$$

   where μ_i is the chemical potential of species i and $'$ and $''$ respectively identify parameters of the actual iteration.

5. Calculation of the parameters D_i is shown in Eq. (3).

$$D_i = n_i' \cdot \left(\mu_i' - \sum_{j=1}^{M} \Theta_j \cdot \alpha_{ji} \right) \quad (i = 1, 2, \ldots N) \tag{3}$$

6. Calculation of the Lagrangian multiplier γ. The sign in Eq. (4) is chosen to make the Gibbs energy of the system tend to a more negative value.

$$\gamma = \pm \left(\sum_{i=1}^{N} D_i^2 / \sigma^2 \right)^{1/2} \tag{4}$$

   where σ is the step-size parameter of the thermodynamic iteration.

7. Calculation of the new number of moles n'' of the species i uses the Eq. (5).

$$\delta\xi_i = D_i/\gamma \qquad n_i'' = n_i' \cdot e^{\delta\xi_i} \qquad (i = 1, 2, \ldots N) \tag{5}$$

   It is obvious that species with an initial concentration of zero cannot be considered within the calculation. Therefore, for all possibly growing species with zero concentration a very low start-value of concentration must be chosen.

8. Unfortunately, the algorithm shifts the mass balance. It is the purpose of steps 8–12 to correct this deviation. At first the actual elemental abundance N'_j of the species j is calculated as shown in Eq. (6).

$$N_j' = \sum_{i=1}^{N} \alpha_{ji} \cdot n_i'' \quad (j = 1, 2, \ldots M) \tag{6}$$

9. Calculation of the parameters Δ_j is shown in Eq. (7).

$$\Delta_j = N_j - N_j' \quad (j = 1, 2, \ldots M) \tag{7}$$

10. To solve for the Lagrangian multipliers ϕ_j, Eq. (8) is used.

$$\sum_{j=1}^{M} \left(\sum_{i=1}^{N} \alpha_{ki} \cdot \alpha_{ji} \cdot n_i''^{\,2} \right) \cdot \phi_j = -\Delta_k \qquad (k = 1, 2, \ldots M) \tag{8}$$

11. Calculation of the parameters E_i is shown in Eq. (9).

$$E_i = \sum_{j=1}^{M} \phi_j \cdot \alpha_{ji} \cdot n_i'' \quad (i = 1, 2, \ldots N) \tag{9}$$

12. Calculation of the new number of moles of the species i is shown in Eq. (10).

$$\delta\xi_i = -E_i \qquad n_i' = n_i'' \cdot e^{\delta\xi_i} \qquad (i = 1, 2, \ldots N) \tag{10}$$

13. Check whether the iteration can be stopped. The iteration is stopped when all parameters D_i remain under a defined limit or if the number of iterations exceeds a limiting value. This criterion is more practicable than a limiting value of γ, indicated by Storey and Van Zeggeren.

14. If not, repeat the iteration, beginning with step 2.

In some cases, deviations from the electric neutrality of the pore solution are possible. It is possible to solve this problem in the following way. First the algorithm is started as described above. Solved species are not calculated, giving them a great positive chemical potential. In a second step, the algorithm is started once more using the original chemical potentials. In contrast to the algorithm described above only the concentrations of the neutral species are calculated. The concentrations of the ions are determined by using the quantity of the reacted neutral species and a list of the reaction equations of the dissolving reactions. In this case the iteration is stopped if the sum of the parameters A does not decrease any further, as calculated by Eq. (11).

$$A_k = \left| \sum_{i}^{N} \mu_i - \sum_{j}^{M} \mu_j \right| \tag{11}$$

where N are the species on the left side of reaction equation k and M are the species on the right side of reaction equation k.

Normally the calculation is restricted to a concentration range of about eight orders of magnitude. If necessary, the range of calculable concentrations can be extended by the following procedure. First an active concentration range is chosen (e.g., five orders of magnitude) and the thermodynamic stable phase assemblage is calculated. The upper limit of the active concentration range must be greater than the highest possible concentration of a species. In the next step the limits of the active concentration range are decreased by one order of magnitude. Concentrations higher than the upper limit of the active concentration range are cut off. The active concentration range is step by step shifted over the total concentration range.

1.2. Consideration of chemical kinetics

Whether a chemical reaction takes place is stated by the thermodynamic calculation. But thermodynamics give no information about the rate of a chemical reaction. The reaction rate must be calculated by the laws of chemical kinetics. The consideration of chemical kinetics and the module for the calculation of the transport processes are the basis for the simulation of nonequilibrium states and processes. Whenever it is possible to describe the concentration changes of one species during a reaction by the laws of the chemical kinetics of heterogenous reactions of the first order, the chemical kinetics of this reaction could be considered within the simulation program presented here. The different chemical reactions are identified and controlled by reaction-specific concentration changes, for example the decrease of SO_4^{2-} in the pore solution and the increase of the ettringite concentrations in the case of a sulphate attack. The basic equation for the calculation of the time-dependent concentration of a species in the case of a heterogenous reaction of the first order is shown in Eq. (12):

$$\Delta c_t = \Delta c_0 \cdot e^{-k \cdot S \cdot t} \tag{12}$$

Δc_t and Δc_0 are the difference between the actual concentration of the species and the equilibrium concentration at the time t and $t = 0$; k is the rate constant; S is the fraction S_s/V where S_s is the reactive surface of the solid and V is the volume of the liquid or gaseous phase in contact with S_s. For the description of the chemical kinetics of corrosive reactions within the pore system of the materials it was necessary to extend Eq. (12) to Eq. (13):

$$\Delta c_t = \Delta c_0 \cdot \Big[(Kc_{new} \cdot KT_{cap} + Kc_{old} \cdot Kca_{cap}) \cdot e^{-k \cdot S_{cap} \cdot \Delta t} + (Kc_{new} \cdot KT_{dif} + Kc_{old} \cdot Kca_{dif}) \cdot e^{-k \cdot S_{dif} \cdot \Delta t} \Big] \tag{13}$$

This equation takes into account the different reactive surfaces in the case of a diffusive and a capillary transport. S_{cap} is the fraction S_s/V accessible during a capillary transport of solved species; S_{dif} is the fraction S_s/V accessible during a diffusive transport; Δt is the width of the time step. Within the simulation program, t and $t = 0$ mean the situation at the end and at the onset of a time step, respectively. It is important to note that the rate constant k used here is not influenced by transport processes within the solid. The parameters KT_{cap} and KT_{dif} are the transported quantities (capillary and diffusive) of the species related to the total transported quantity of these species [see Eq. (14)]:

$$KT_{cap} = \Delta c_{cap} / \Delta c_{total} \qquad KT_{dif} = \Delta c_{dif} / \Delta c_{total} \tag{14}$$

The parameter Kc_{new} is that part of Δc_0 that was added since the last time step. Kc_{old} is that part of Δc_0 that was already existing [see Eq. (15)]. Kc_{old} equals Δc_t of the preceding time step.

$$Kc_{new} = \Delta c_{0,new} / \Delta c_0 \qquad Kc_{old} = \Delta c_{0,old} / \Delta c_0 \tag{15}$$

The parameters Kca_{cap} and Kca_{dif} are those parts of $\Delta c_{0,\mathrm{old}}$ that are located in the pores that can be reached by capillary and diffusive transport processes, respectively. They are defined by the following equations. For the calculation of these parameters the data of the preceding time step must be used [see Eq. (16) and Eq. (17)]:

$$Kca_{cap} = \Delta c_0 \cdot (Kc_{new} \cdot KT_{cap} + Kc_{old} \cdot Kca_{cap}) \cdot e^{-k \cdot S_{cap} \cdot \Delta t} \tag{16}$$

$$Kca_{dif} = \Delta c_0 \cdot (Kc_{new} \cdot KT_{dif} + Kc_{old} \cdot Kca_{dif}) \cdot e^{-k \cdot S_{dif} \cdot \Delta t} \tag{17}$$

These parameters are pairwise normalized to 1.0. Kinetic calculations within the simulation program are made as follows. At first, the thermodynamic stable phase assemblage is calculated. The concentration difference Δc_0 is the difference between the concentration at the end of the calculation of the transport processes and the equilibrium concentration. With Eq. (13) the concentration difference Δc_t to the equilibrium phase assemblage is calculated. The concentration of the species is, under consideration of thermodynamics and kinetics, the sum of the equilibrium concentration and the concentration difference Δc_t. This concentration is named $c_{\mathrm{thermo,kinetics}}$. Finally, the thermodynamic calculation is repeated. If the concentration of a species that is involved in the kinetic calculation intersects $c_{\mathrm{thermo,kinetics}}$, the concentration is fixed at this value. During the following iterations, the concentrations of these species in the Eqs. (2), (3), (8), and (9) are set to zero. An exact calculation of the temperature dependence of the rate constants by the equation of Arrhenius is not included in the simulation. The model uses the rule of thumb, that the rate of chemical reactions is doubled if the temperature is increased by 10°K.

2. Calculation of the transport processes

It is possible to calculate the following transport processes within the simulation: capillary suction of a solvent and solved ions/neutral species, diffusion of any number of solved species (including the influence of the diffusion potential caused by the different diffusion velocities of the ions), isothermal water vapor diffusion, and diffusion of solved species through the inner surface of cracks. We use a simple explicit finite difference method for the numerical calculation. The following equations describe the concentration changes Δc due to transport processes through the surface between two volume elements in mol/m^3 during the time increment Δt. The calculated transported concentrations are added. The magnitude of each time increment is automatically adapted to obtain maximum speed.

2.1. Water vapour diffusion

Water vapour diffusion is shown in Eq. (18).

$$\Delta c_{FDP} = \frac{\Delta t}{\Delta x_1} \cdot \frac{\rho_w}{M_{m,w}} \cdot FDP \cdot \frac{\Delta \varphi}{\Delta x_2} \tag{18}$$

where FDP is the isothermal water vapour diffusion coefficient [13] in the contact plane of two volume elements. The moisture dependence has to be determined experimentally or on the basis of literature data. The temperature dependence of FDP is calculated according to Kießl [13]. Δx_1 is the dimension of the actual volume element. Δx_2 is the distance between the centres of adjacent volume elements. ρ_w is the density of water. $M_{m,w}$ is the molar mass of water. $\Delta\varphi$ is the difference of the relative humidities, φ is calculated from the water content by using the sorption isotherm.

2.2. Capillary suction

Capillary suction is shown in Eq. (19).

$$\Delta c_{FKU} = \frac{\Delta t}{\Delta x_1} \cdot \frac{\rho_w \cdot u_f}{M_{m,L}} \cdot FKU \cdot \frac{\Delta(u/u_f)}{\Delta x_2} \tag{19}$$

where *FKU* is the water transport coefficient (capillary, grad u [13]) in the contact plane between the two volume elements. The temperature dependence of *FKU* is calculated according to Kießl [13]. u is the water content. u_f is the free-water content (saturation water content without pressure). $M_{m,L}$ is the molar mass of the solvent.

The moisture dependence of *FKU* is approximately calculated by the following equation. FKU_f is calculated from the water absorption coefficient and the free-water content according to Kießl. FKU_f/FKU_0 is assumed as 10^4 [13]. See Eq. (20).

$$FKU(u) = FKU_0 \cdot e^{u/u_f \cdot \ln(FKU_f/FKU_0)} \tag{20}$$

The concentration changes of solved ions/neutral species due to capillary suction are calculated by Eq. (21):

$$\Delta c_g = \Delta c_{FKU} \cdot c_g / c_{H_2O} \tag{21}$$

where c_g is the concentration of species g in the actual or in the adjoining volume element (capillary suction out off or into the actual volume element, respectively). c_{H_2O} is the concentration of water in the actual or in the adjoining volume element, respectively.

2.3. Diffusion of solved species

The diffusion of solved species is shown in Eq. (22):

$$\Delta c_{g,dif} = \frac{\Delta t}{\Delta x_1} \cdot M_L \cdot D_g \cdot \frac{\Delta m_g}{\Delta x_2} \tag{22}$$

where D_g is the diffusion coefficient of species g; Δm_g is the difference of molalities (mol/kg solvent) of species g; and M_L is the mass of solvent per m^3.

The temperature dependence of the diffusion coefficients is simulated by an Arrhenius equation. The coefficients are not calculated as a function of moisture. Compared with capillary suction, the diffusion of solved species is a less important transport process. It is only significant in the case of a liquid-saturated material. Therefore, the user should employ coefficients measured for specimens saturated with water. Diffusion coefficients unaffected by chemical reactions should be used, because reactions are simulated by the thermodynamic module.

2.4. Consideration of the influence of the diffusion potential

The different diffusion velocities of the various ions cause a diffusion potential. Assuming that the pore solution of mineral-building materials is not electrically charged, the diffusion potential must lead to an additional concentration change $\Delta c_{g,dp}$. The derivation of Eq. (23) is shown in a previous work [1].

$$\Delta c_{g,dp} = -z_g \cdot D_g \cdot m_g \cdot \frac{\sum_g z_g \cdot \Delta c_{g,dif}}{\sum_g z_g^2 \cdot D_g \cdot m_g} \tag{23}$$

where z_g is the charge of ion g and m is the molality.

2.5. Change of transport parameters by corrosive effects

Corrosion processes alter the pore structure and the porosity of the material and therefore the various transport parameters. The changes of the transport parameters are calculated as follows. During the simulation of a corrosion process the free-water content u_f is actualized in each volume element and at each time step by Eq. (24):

$$u_{f,t} = \frac{v_{sp,t_0} + \epsilon_{w,t_0} - v_{sp,t}}{\epsilon_{w,t_0}} \cdot u_{f,t_0} \tag{24}$$

where t is time t; t_0 is the time at onset of the corrosion process; v_{sp} is the volume fraction of the solid phases (result of the thermodynamic/kinetic module); and ϵ_w is the total open porosity (0 . . . 1).

The free-water content and the open porosity at the beginning of the corrosion process must be estimated or experimentally determined. $\epsilon_{HG,t}$, the total porosity by mercury intrusion, and $\epsilon_{w,t}$ are actualized in the same way. ϵ_v, the air content, is assumed to be constant. The simulation uses the following equations presented by Gaber [14] to calculate actualized water absorption coefficients w and diffusion coefficients D of the solved species g. The free-water content u_f and the water absorption coefficient w are used to calculate the transport coefficient FKU_f as described by Kieβl [13] [Eqs. (25), (26), (27), and (28); all ϵ are in vol%]:

$$w = a_w \cdot \epsilon^{1.5} \cdot \epsilon_v^{-0.25} \qquad D_g = a_D \cdot \epsilon^8 \tag{25}$$

with:

$$a_w = \frac{w_{exp}}{\epsilon^{1,5} \cdot \epsilon_v^{-0,25}} \qquad a_D = \frac{D_{exp}}{\epsilon^8} \tag{26}$$

$$\epsilon = \epsilon_{HG}^{1/4} \cdot (\epsilon_{HG} - \epsilon_v)^{1/4} \cdot \epsilon_w^{1/4} \cdot (\epsilon_w - \epsilon_v)^{1/4} \tag{27}$$

$$\mathrm{D}_{\mathrm{g,\ maximum}} = \mathrm{D}_{\mathrm{g,\ in\ free\ liquid}} \cdot \epsilon_{\mathrm{w}}/100 \tag{28}$$

The factors a are assumed to be constant and calculated with the estimated or experimentally determined coefficients of water absorption and diffusion of the uncorroded material. At present, the simulation model is unable to actualize the transport coefficient *FDP* as a function of porosity and pore structure. For the actualization of transport parameters we do not use equations that imply information belonging to the pore radius distribution because it is not yet possible to simulate the change of distribution of pore radii by a corrosion process.

2.6. Diffusion of solved species through the inner surface of cracks

Some corrosion processes result in the rise of cracks. In this case, it is possible to calculate an additional diffusion process via the inner surface of cracks, into the porous material.

3. Actualization of the material strength

The simulation program actualizes the material strength β for each volume element and each time step. It uses a modified form of the equation of Balshin [15], Eq. (29):

$$\beta = \sum_i v_i \cdot \beta_{c,i} \cdot (1-p)^b \tag{29}$$

where v_i is the volume fraction of species i (result of the thermodynamic/kinetic calculation); $\beta_{c,i}$ is the characteristic strength (theoretical strength at zero porosity) of species i; and p is the total porosity of binder (0 . . . 1, result of the thermodynamic/kinetic calculation). b is determined at the beginning of the simulation for the strength of the uncorroded material; it is assumed to be a constant.

4. Simulation of additional corrosive effects

4.1. Expansion model

For the determination of expansion in case of sulphate attack, a model was developed. This model presupposes that expansion and cracking in case of sulphate attack are caused by the formation of ettringite. The formation of ettringite consumes AFm and $Ca(OH)_2$. The rate of this heterogenous reaction is proportional to the surface of the pores divided by their volume. In the simulation model, the quantity of the newly generated ettringite is distributed in the pores accordingly. The ettringite volume that exceeds the existing pore volume of the respective pore class is added and interpreted as actual expansion of the volume element. The detailed derivation of this model is presented in a previous work [1]. It is not contradictory to the Riecke principle and it is able to explain why there is not necessarily a correlation between the amount of newly generated ettringite and the magnitude of expansion. The pore radius distribution is a decisive parameter for expansion.

4.2. Examination of limiting values

During simulation, several material properties are periodically checked. For example: If the material strength within a volume element decreases below a limiting value, the volume element is removed from the structure. If the expansion within a volume element increases up to a limiting value, the onset of cracks is assumed. Then the strength of the element is set to zero and an additional diffusion process through the cracks is calculated.

5. Discussion

An algorithm for the simulation of the corrosion of mineral-building materials is described. It combines the calculation of transport processes with the quantitative simulation of chemical reactions. The experimental verification of the model is discussed in the second part of this paper. At the present, from the mathematical point of view, the model is not capable to deal with the following items:

- It is not possible to calculate the sorption isotherms and the transport coefficients *FDP* as a function of the porosity and pore structure. For the actualization of these transport parameters, it is necessary to simulate the change of distribution of pore radii by the various corrosion processes.
- The simulation of transport processes caused by pressure gradients (permeation) is not possible.
- The effect of cracks on transport processes is only considered in the case of the diffusion of solved species. During a sulphate attack, the formation of cracks and the crack volume is simulated by the algorithm, but the number of cracks per area must be estimated by the operator.
- Only species with known thermodynamic data of high quality can be considered within the simulation. The simulation of corrosion processes at elevated pressure is restricted to hydrostatic pressure.
- The dispersion of the onset data cannot be considered within the model. It is deterministic.
- At present, the algorithm is extended, so that the calculation of two-dimensional transport processes, the simulation of heat transport-processes, and the calculation of transport processes caused by thermal gradients become possible.

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