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Cellular automata approach to hybrid surface and diffusion controlled reactions

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Abstract

Cellular automata are frequently used to model chemical reactions and processes. In this paper, a direct relation is established between chemical kinetic models for surface and diffusion controlled reactions and cellular automata parameters. The considered particles are allowed to have growing/shrinking sizes, caused by the difference in the volume of the consumed reactant and the formed reaction product. From the moment a minimum diffusion layer thickness is obtained, the cellular automata approach can be applied to study the diffusion (ash layer) controlled model for both cases. In order to be able to also describe the reaction before this minimum diffusion layer thickness is formed, chemical reaction controlled and diffusion controlled models are combined here. Applying this hybrid model, a closed-form relation is found between the cellular automata parameters (particle size, reaction probability) and the fundamental kinetics of surface (β_1) and diffusion (β_2) controlled reactions.

Keywords Reaction kinetics · Cellular Automata · Chemical reaction kinetics · Diffusion controlled · CEMHYD3D

Abbreviations

CRC	Chemical reaction controlled model
CA	Cellular automata
SCM	Scrinking (unreacted) core model
PCM	Progressive core model

Latin

C	Concentration
C	Cycle Number

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C_e	Effective concentration
C_{tr}	Number of Cycles at the transition from chemical to diffussion controlled reaction
D_e	Effective diffusion coefficient
k_1	Kinetic parameter for the chemical reaction model
k_2	Kinetic parameter for the diffusion controlled model
P_0	Basic dissolution probability of a voxel
P_1	Dissolution probability of a voxel in the chemical reaction controlled phase
P_2	Dissolution probability of a voxel in the diffusion controlled phase
r_0	Initial radius of the particle
r_c	Radius of the unreacted core of a particle
$r_{c,tr}$	Radius of the unreacted core of a particle at the transition point
r_e	Outer radius of the particle including the ash/product layer which is formed
r_p	Radius of the particle in cellular automata
t	Time
t_{tr}	Point in time of the transition from chemical to diffusion controlled reaction
v	Volume ratio of product formed to the reacted reactant
V_0	Initial volume of the particle at $t = 0$
V_c	Volume of the unreacted core of a particle
V_e	Total volume of a particle including the ash/product layer which is formed

Greek

α	Reaction degree
α_{tr}	Reaction degree at the transition from chemical to diffusion controlled reaction
β_1	Relation constants for linking the chemical reaction controlled model to cellular automata model
β_2	Relation constants for linking the diffusion controlled model to cellular automata model
δ	The layer thickness of the ash/product layer
δ_{tr}	The layer thickness at the transition point
τ_1	Time needed for full conversion/reaction/hydration time ($\alpha = 1$) in the chemical reaction controlled model
τ_2	Time needed for full conversion/reaction/hydration time ($\alpha = 1$) in the diffusion controlled model
τ_3	Time needed for full conversion/reaction/hydration time ($\alpha = 1$) in the hybrid model

Introduction

Chemical reactions have been studied for hundreds of years. Reactions can be described based either on spatial and temporal progression of reactions in solids. The progression of chemical reactions by chemical reaction engineering theorists is typically performed using spherical models in an infinite space. Besides these models also other methods have become available such as cellular automata (CA), which enable the reaction simulation of arbitrary shaped and densely packed particles.

Cellular automata are therefore already commonly used for the modeling of chemical systems [1–11]. Cellular automata systems are among others applied for studying biology, cement reaction, population growth, computability theory, mathematics, physics, complexity science, theoretical biology and microstructure modelling. In [12], the focus was on the application of the cellular automata approach to study the chemical reaction controlled model, which can for instance be found in [13]. A unique relation between the simulations using cellular automata approach and chemical reaction controlled model was established [12, 14].

In many reactions, however, a layer of reaction products is formed on the unreacted core, and the so-called diffusion model then applies [13, 15–17]. The present article, part of a larger study [14], addresses the situation, in which the reaction product will precipitate on the surface of the unreacted core. Hereby two situations are considered, i.e. in the first case the volume of the reaction product equals the volume of the consumed reactant ($v = 1$) ("Constant particle size" section) and in the second case the volume of reaction product is unequal to the volume of reactant ($v \neq 1$) ("Varying particle size case" section). This is done using the combination of a chemical reaction controlled model and a diffusion controlled model. Due to the discrete nature of cellular automata, the start of the reaction is still chemical reaction controlled, since first a certain—discrete—layer thickness needs to be formed. Therefore, a hybrid model is introduced in this paper ("Hybrid model" section) of which the first phase is chemical reaction controlled and second phase is ash diffusion controlled. This hybrid model is a combined application of the already known models from literature. The relation between general reaction kinetic models and cellular automata is of interest for the further improvement of cellular automata reaction models. Since reactions often follow the shrinking core model, cellular automata models need to be able to model these reactions. In this paper, part of PhD-study of the corresponding author [14], closed-form relations are derived between fundamental chemical properties of diffusion controlled reaction on the one hand, and cellular automata parameters on the other.

Chemical reaction models

Introduction

In the literature of chemical kinetics, two approaches can be distinguished: the zone reaction model or progressive-conversion model (PCM) [18] and the shrinking unreacted core model (SCM). Within the progressive-conversion model, the solid reactant is converted continuously and progressively throughout the particle within the PCM, while the reactions according to the SCM take place on the outer skin of the particle and the zone of reaction is moving into the solid leaving behind completely converted material and inert solids.

The two reaction kinetic approaches can be considered as the two limiting cases of the reality and actually a combination of both models should be applied [19].

Therefore the model of Ishida et al. considers the shrinking core model as a special case of the progressive conversion model [18, 20].

Three resistances to reaction can be distinguished namely, film diffusion, ash diffusion and reaction controlled (surface area controlled). The rate-controlling step is determined by the highest resistance of these three [21–23].

Within the SCM, the assumption of unchanging or changing particle size is crucial, since it determines the available reaction surface. This assumption has largest influence in the film diffusion-controlled system. In the case of the unchanging particle size, the surface area of the original particle is used, while in the changing particle size case the surface area of the unreacted core is used.

Both the SCM and PCM reaction models are considered to have a single reaction mechanism as dominant. In practice, often a combination of reaction mechanisms are present. Di Liddo and Stakgold [24] introduced a model for the combustion of a porous solid with two moving fronts, one of which is distributed through the entire porous solid and the other of which has partial conversion ahead of it. Braun et al. [19] introduced a reaction model for a flat solid particle with two reactions with the fluid at two moving boundaries. A diffusion-controlled reaction creates an ash layer in the particle according to the unreacted core shrinking model. The second process burns off this ash layer (resulting in the shrinkage of the whole particle) and the process is chemical reaction controlled. Braun et al. [25] give an analytical solution for the equations in this reaction system using a Lambert W function. Ogata et al. [26] and Homma et al. [27] give a similar system for spherical particles. Unlike the model presented by Braun et al. [19, 25] for two dimensional Cartesian coordinates, the model of Ogata and Homma cannot be solved analytically. Therefore, Homma et al. solve their equations numerically and using the Euler method with a very small interval for the partial reaction degree. Therefore their method cannot directly be applied. In this paper a different approach is used, which enables the analytical solution of the system but lacks some sophistication of the method of Braun et al. [19] and Ogata et al. [26] for plates and spheres, respectively. Nevertheless the method introduced here has sufficient reliability.

The chemical reaction controlled mechanism, sometimes also referred to as phase-boundary mechanism, was related to cellular automata parameters. This paper deals with the hybrid system; this system is chemical reaction controlled (CRC) until the so-called transition point and becomes diffusion controlled from there onwards. The transition point (δ_{tr}) is the moment an ash/product layer of certain thickness (the so-called δ_{tr}) is formed. Fig. 1 provides a graphical overview of the studied system. Besides the thickness of ash/product layer, this point can be described by the time needed to reach this point t_{tr}, the radius of the unreacted core r_c and the reaction degree α_{tr}. In the CRC model, the formed reaction products do not play a role, since the reaction is surface controlled. In this paper, a hybrid system is studied and for this system, the reaction product is relevant and therefore considered here.

Fig. 2 shows a graphical representation of a particle with ash layer formation. The model assumes that the reaction rate at any moment is given by its rate of diffusion to the reaction surface. The volume including ash layer is:

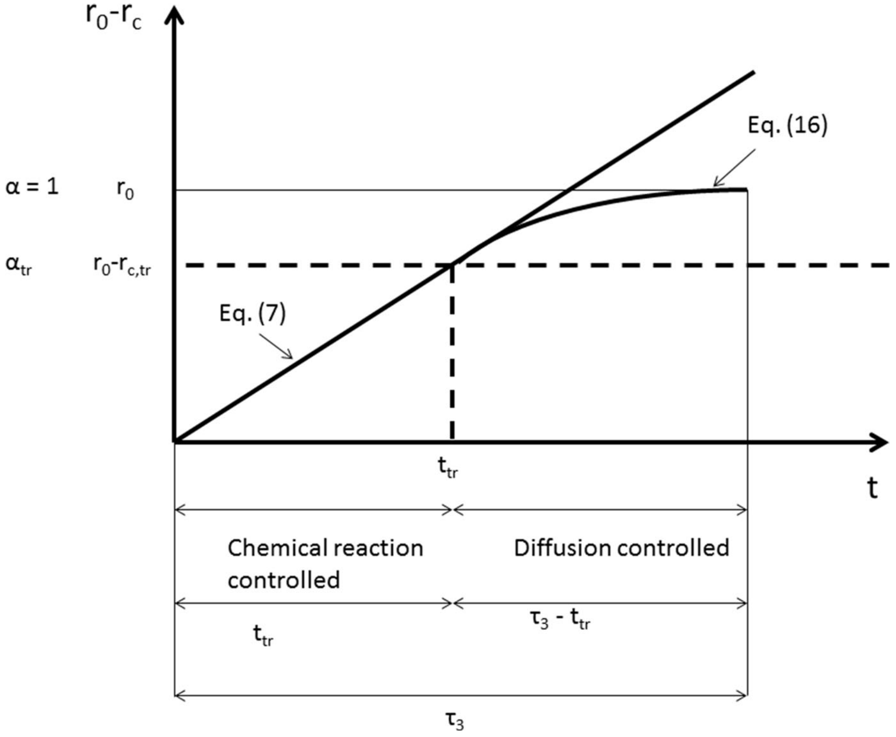


Fig. 1 The relationship between basic rate factor, diffusion coefficient and transition point (t_{tr}, $r_{c,tr}$) (modified from van Breugel)

$$V_e = V_c + v(V_0 - V_c). \tag{1}$$

Here v constitutes the volume increase ratio associated with the reaction (V_e/V_0), V_0 is the volume of the initial particle with radius r_0, V_C is the volume of the shrinking core (with radius r_c) and V_e is the volume of the particle including ash layer (with radius r_e). Based on this volume relationship, the radius of varying particle including ash layer can be derived:

$$r_e^3 = vr_o^3 + (1 - v)r_c^3. \tag{2}$$

The reaction degree can be described based on the volume of the unreacted core (V_c) and initial volume of the particle (V_0). The equation for the reaction degree is:

$$\alpha = 1 - \frac{V_c}{V_0} = 1 - \left(\frac{r_c}{r_0}\right)^3. \tag{3}$$

Here r_c is the radius of the shrinking core and r_0 the initial radius of the particle.

The transition point between the surface and diffusion controlled phase within the reaction can be described by several parameters, such as time, reaction degree, radius of shrinking core and product/ash layer thickness. Taking the layer thickness

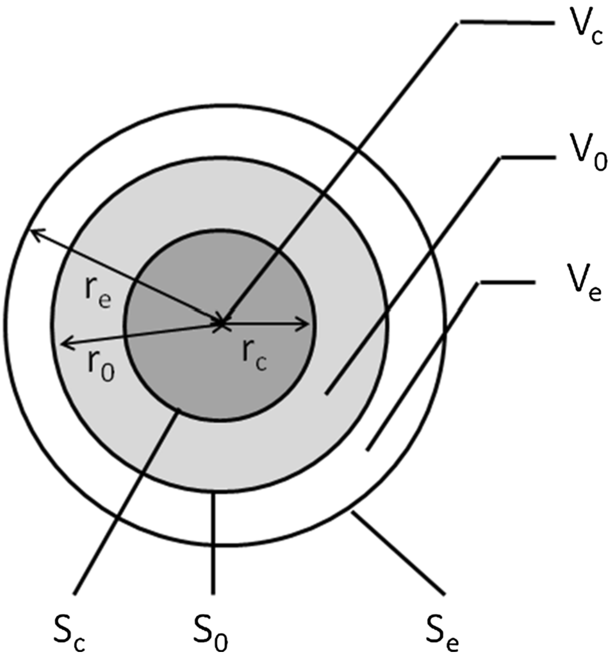


Fig. 2 Graphical representation of the ash diffusion system

(δ_{tr}) and radius of the unreacted core ($r_{c,tr}$) as a starting point, the corresponding reaction degree at the transition point is:

$$\alpha_{tr} = 1 - \left(\frac{r_{c,tr}}{r_0}\right)^3. \tag{4}$$

Furthermore, the (external) radius of particle including product/ash layer at the transition point can be described based either on volume increase ratio v or the transition layer thickness (δ_{tr});

$$r_{e,tr} = \sqrt[3]{v r_0^3 + (1 - v) r_{c,tr}^3} \tag{5}$$

$$r_{e,tr} = r_{c,tr} + \delta_{tr}. \tag{6}$$

The following "Chemical reaction controlled and "Diffusion controlled" sections address the chemical reaction controlled and diffusion controlled stage, respectively, while "Hybrid model" section combines both stages to a single (hybrid) model.

Chemical reaction controlled

The general equation [13, 16] for the chemical reaction controlled system, as also presented in [12], is:

$$\frac{t}{\tau_1} = 1 - \frac{r_c}{r_0} = 1 - (1 - \alpha)^{1/3} \quad \text{with } \tau_1 = \frac{r_0}{k_1}. \tag{7}$$

Here α is the reaction degree, t is the reaction time, τ_1 is the time needed for full reaction ($\alpha = 1$), k_1 is the reaction rate constant and r_0 is the initial radius of the particle.

In "Introduction" section, the transition point was introduced. The time needed for reaching the transition point t_{tr} can be described using the chemical reaction controlled model (Eq. 7) is:

$$t_{tr} = \left(1 - \frac{r_{c,tr}}{r_0}\right) \cdot \tau_1 = \left(1 - (1 - \alpha_{tr})^{1/3}\right) \cdot \tau_1. \tag{8}$$

One can notice that for $\alpha_{tr} = 1$, t_{tr} equals τ_1, which means that the conversion is completely chemical reaction controlled.

Diffusion controlled

As a first step only the diffusion model is considered. The chemical reaction controlled model assumes that the formed ash/product, if any, does not limit the reaction speed. The formed ash/product, however in practice, can reduce the reaction rate. The ash-layer model deals with this resistance to reaction. Šesták and Berggren [28] mention two three-dimensional transport process models, namely the Jander model [29] and the Ginstling and Brounshtein model [30]. The Jander model assumes a spherical reactant surface and flat product layer, while the Ginstling-Brounshtein model assumes a spherical reactant surface as well as spherical product layer. Carter [31] points out that there are some major simplifications in the Jander model. The Jander equation assumes a plane surface which is only valid when the ratio of inner and outer radius of the ash layer is close to unity, so for small values of α. Brown [32] points out that the Jander model cannot account for the decrease in interfacial area between the reactant and the reaction product as reaction proceeds. Considering these limitations of the Jander model, the model of Ginstling and Brounshtein [30] is used in the present paper.

The equations of Ginsling and Brounshtein [30] have also been used by Levenspiel [13, 15] to describe the reaction of a shrinking core with an ash layer, where the total size of the particle (reacted and unreacted) is constant. The model assumes that the reaction rate at any moment in time is given by its rate of diffusion to the reaction surface:

$$-\frac{dV_c}{dt} = A_e Q. \tag{9}$$

Here Q is the flux of A_e through the exterior surface of a particle. The rate of diffusion depends on the effective diffusion coefficient (D_e) and the concentration (C_e) present on the reaction surface:

$$Q = D_e \frac{dC}{dr}. \tag{10}$$

Combining Eqs. 5, 9 and 10, using $A_e = 4\pi r_e^2$ and integrating by applying C = 0 for r_c, $C = C_e$ for $r = r_e$ leads to:

$$-\frac{dV_c}{dt} = 4\pi D_e C_e \left(r_c - \left(v \cdot r_0^3 + (1 - v) \cdot r_c^3 \right)^{1/3} \right). \tag{11}$$

Using $V_c = 4/3\pi r_c^3$, separating of the variables r_c and t leads to:

$$\frac{dr_c}{dt} = \frac{D_e C_e \left(r_c - \left(v \cdot r_0^3 + (1 - v) \cdot r_c^3 \right)^{1/3} \right)}{r_c^2}. \tag{12}$$

Integrating Eq. 12 and applying $r_c(t = 0) = r_0$, and combining with Eq. 3 leads to:

$$\frac{k_2 t}{r_0^2} = \frac{v - (v + (1 - v)(1 - \alpha))^{2/3}}{v - 1} - (1 - \alpha)^{2/3}. \tag{13}$$

Here α is the reaction degree and k_2 is the kinetic constant. The kinetic parameter k_2 describes the effective diffusion coefficient (D_e) and the concentration of the solution at the reaction surface (C_e). For the complete conversion of a particle, $r_c = 0$, the total reaction time (τ_2) required equals:

$$\tau_2 = \frac{v - v^{2/3}}{v - 1} \cdot \frac{r_0^2}{k_2}. \tag{14}$$

So, the dimensionless equation for this system is:

$$\frac{t}{\tau_2} = \left(\frac{v - (v + (1 - v)(1 - \alpha))^{2/3}}{v - 1} - (1 - \alpha)^{2/3} \right) \cdot \left[\frac{v - 1}{v - v^{2/3}} \right]. \tag{15}$$

This equation is also given by Szekely [16] and Ghoroi and Suresh [33] for the diffusion controlled reaction of particles with changing size based on the work of Carter [31]. In case of v = 1, Eq. 15, turns into the ash diffusion equation of Levenspiel [13], using the L'Hôspital's rule. This ash diffusion equation of Levenspiel is:

$$\frac{3t}{\tau_2} = 1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha). \tag{16}$$

Hybrid model

The model in the previous subsection is applicable when during the whole conversion (i.e. $0 \leq \alpha \leq 1$), the diffusion control model is applicable. But in cellular automata systems, the process starts with chemical reaction controlled, and after the formation of a layer, diffusion controlled kinetics prevails. So, for $0 \leq \alpha \leq \alpha_{tr}$, CRC from "Chemical reaction controlled" section prevails and for $\alpha_{tr} \leq \alpha \leq 1$, diffusion ("Diffusion controlled" section) is governing the reaction speed. The time corresponding to α_{tr} is called t_{tr}.

Fig. 1 shows a graphical representation of the studied system. As one can notice, the total reaction time τ_3 consists of two parts. The first part of the reaction is chemical reaction controlled. This part is valid until a transition thickness δ_{tr} is reached. The time required for this stage is given by Eq. 8.

The second part of the reaction is diffusion controlled. To determine the time needed for this phase, Eq. 12 needs to be integrated with applying $r_c = r_{c,tr}$ for $t = t_{tr}$. After integration and simplification, this leads to:

$$(t - t_{tr})\frac{k_2}{r_0^2} = -\frac{(v + (1 - v)(1 - \alpha))^{2/3}}{v - 1} - (1 - \alpha)^{2/3} + \frac{(v + (1 - v)(1 - \alpha_{tr}))^{2/3}}{v - 1} + (1 - \alpha_{tr})^{2/3}. \tag{17}$$

One can notice the resemblance of Eqs. 7–13. In the case of $\alpha_{tr} = 0$ and $t_{tr} = 0$, Eq. 17 transforms into Eq. 13. In fact, Eq. 17 is the difference between the results of Eq. 13 for t_{tr} and t. For v = 1, Eq. 17 becomes:

$$(t - t_{tr})\frac{k_2}{r_0^2} = 3(1 - \alpha_{tr})^{2/3} - 3(1 - \alpha)^{2/3} + 2(\alpha_{tr} - \alpha). \tag{18}$$

Using Eq. 8 for the transition time and substituting $\alpha = 1$ into Eq. 17 for the diffusion controlled stage, the time τ_3 needed for full reaction ($\alpha = 1$) is:

$$\tau_3 = \frac{-v^{2/3} + (v + (1 - v)(1 - \alpha_{tr}))^{2/3} + (v - 1)(1 - \alpha_{tr})^{2/3}}{v - v^{2/3}}\tau_2 + \left(1 - (1 - \alpha_{tr})^{1/3}\right)\tau_1. \tag{19}$$

For $\alpha_{tr} = 0$ (i.e. the system is fully diffusion controlled), τ_3 is equal to τ_2 and for $\alpha_{tr} = 1$ (i.e. the system is complete chemical reaction controlled), τ_3 is equal to τ_1, as would be expected.

In the case of v = 1 and using the L'Hôspital's rule, Eq. 19 can be rewritten as:

$$\tau_3 = \left(3(1 - \alpha_{tr})^{2/3} - 2(1 - \alpha_{tr})\right)\tau_2 + \left(1 - (1 - \alpha_{tr})^{1/3}\right)\tau_1. \tag{20}$$

For $\alpha_{tr} = 0$ (i.e. the system is fully diffusion controlled), τ_3 is equal to $3/\tau_2$ and for $\alpha_{tr} = 1$, τ_3 is equal to τ_1.

Cellular automata approach

The background of cellular automata has been illustrated in [12, 14]. Cellular automata can be best described as a tool for the simple mathematical idealizations of natural systems [34]. In this article, a cellular automaton is used to represent a system in which a particle reacts and a reaction product is formed. Furthermore, a direct unique relation between the ash diffusion model of the previous section and a CA approach is sought. As a tool for the cellular automata simulations, a modified version of CEMHYD3D [35–38] is used in this study. In [12], a general and original linear relation between the cellular automata parameters and chemical reaction model parameters were established for the case in which reaction products are absent in the system. In the present paper, a system with the formation of reaction product layer (ash layer) through which diffusion needs to take place, is studied. Therefore, the diffusion resistance of the product/ash layer needs to be taken into account. In the case of no reaction product formed on the shrinking core [12], the reaction probability remains the same for all α (i.e. $P_1 = P_0$, with P_0 the basic (unmodified) dissolution probability). But in case of the presence of an ash layer, the reaction probability is depending on the layer thickness (δ) and reads analogue to [37, 39]:

$$P_2 = P_1 \frac{\delta_{tr}}{\delta}. \tag{21}$$

In this equation, the transition thickness (δ_{tr}) is also introduced, since first an ash layer needs to be formed. Up to the moment a pre-determined layer thickness (δ_{tr}) is reached, the reaction is chemical reaction controlled and after this point the reaction is considered to be diffusion controlled. Fig. 1 shows the principle of this hybrid system. In this hybrid system, the system is reaction controlled until an ash layer of minimal one voxel is formed. This is inherent to the cellular automata approach, in which the reaction is simulated using discrete voxels. In the cellular automata approach, it is possible to use layer thickness of more one voxel, but layer thickness smaller than unity is impossible due to discrete manner of the cellular automata approach. Besides the discrete case, one can also derive the corresponding radius of the unreacted core for the continuous case by solving Eqs. 5 and 6. The combination of these equations leads to the following implicit equation:

$$r_{c,tr} = \sqrt[3]{v r_0^3 + (1 - v) r_{c,tr}^3} - \delta_{tr}. \tag{22}$$

The value for $r_{c,tr}$ can be approached using the following equation:

$$r_{c,tr} = r_0 - \frac{\delta_{tr}}{v}. \tag{23}$$

The corresponding reaction degree (α_{tr}) for an approximated radius is:

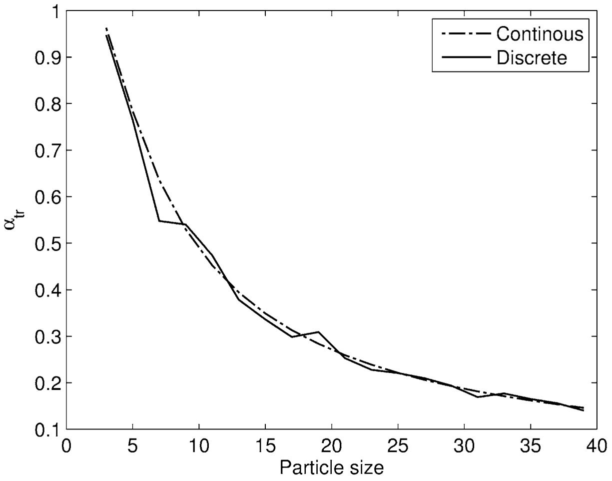


Fig. 3 Transition reaction degree for the transition of chemical reaction controlled to diffusion controlled

$$\alpha_{tr} = 1 - \left(1 - \frac{\delta_{tr}}{v r_0}\right)^3. \tag{24}$$

For the discrete case, as the case in the cellular automata models, the formed layer needs to equal an integer and α_{tr} is in general higher than that of the continuous case (Fig. 3).

Simulations results

In [12], the reaction controlled system, in which the presence of the reacted/dissolved voxels is not relevant, was studied. For the (ash) diffusion controlled model, however, the reaction products on the surface of reactive material are relevant and need to be included. The system uses the diffusion layer reaction mechanism as described in the previous section with δ_{tr} = 1 μm.

Similarly to the previous analysis of the reaction controlled system [12], a series of 165 simulations has been performed with reaction probabilities in the range of 0.003–0.099 and digitized particle sizes d of 7, 13, 21, 25 and 35, respectively. The particle shape has been modified in the same way as in [40]. This modification improves sphericity and roundness of the digitized particles, which approaches a spherical shape better. Based on the results, a linear relation between the presented ash layer model and cycle number is determined for each simulation.

Chemical reaction controlled stage

In the first stage of the reaction, the system is chemical reaction controlled. In our previous paper [12], a linear relation between cycles, particle size and reaction probability is derived. This relation is:

Table 1 The derived values of β_1 for d = 7, 13, 21, 25 and 35 and different values of v for the chemical reaction controlled phase up to α_{tr}

v	β_1
0	1.360
1	1.314
1.05	1.313
1.35	1.314
1.7	1.310
2.5	1.313
3.4	1.313
4.25	1.315
5.1	1.315
5.95	1.314
6.8	1.314

$$t = \beta_1 \frac{P_0}{k_1} \cdot \frac{r_0}{r_p} \cdot (C - 2). \tag{25}$$

Here β_1 is the relation constant for CRC, r_p the radius of particle size in voxels and P_0 the dissolution probability. Using the fitting toolbox of Matlab®, the β_1 are determined based on the linear regression between time (Eq. 7) and cycles ((C-2)·P_0/r_p). For this regression analysis, the values for r_0, r_p, P_0, k_1 are the input variables, corresponding to the different simulations. This relation is tested here for $0.05 < \alpha < \alpha_{tr}$ with α_{tr} being the transition reaction degree as defined in the previous section. For the $v \geq 1$ system, a value of 1.31 was found (Table 1), while for v = 0, a value of 1.36 was obtained for the same range.

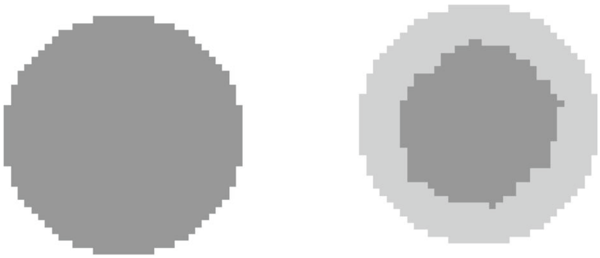
Constant particle size

Fig. 4 shows the reaction of a 35 particle using the new reaction routine described in [12, 14]. One can notice from this figure that the particle indeed remains the same and that no cavity is formed between the ash/product-layer and the (unreacted) shrinking core.

In the ideal situation, the simulation curves follow the diffusion controlled model from cycle C_{tr} onwards. In [12], the cellular automata cycles were correlated to the chemical reaction controlled model based on the reaction degree. Here the same approach is followed for the diffusion controlled model from C_{tr} and α_{tr} onwards. Therefore, the relation equation on Eq. 16 is:

$$3(1-\alpha_{tr})^{2/3} - 3(1-\alpha)^{2/3} + 2(\alpha_{tr} - \alpha) = \beta_2 (C - C_{tr}) \frac{P_0}{r_p^2}. \tag{26}$$

Here β_2 is the relation constant, C_{tr} is the cycle in which the (discrete) transition reaction degree α_{tr} is reached, r_p the radius of particle size in voxels and P_0 the reaction probability. Table 2a shows the results based on the ash layer model of Levenspiel (Eq. 16) for the reaction degree between α_{tr} and 0.9 for d = 13, 21, 25



Cycle 1 Cycle 1000

Cycle 200 Cycle 3000

Cycle 4000 Cycle 4798

Fig. 4 Example of dissoluting particle and the developing shape during its reaction in case of v = 1 (in red the unreacted core and in blue the formed reaction product)

and 35. During the determination of the relation, a coefficient of variation of 0.02 was found, which is half of the coefficient of variation found in [12] for the chemical reaction controlled model for shrinking particles (0.04).

Table 2b shows the results of determining the β_2 of 10 simulations with the same initial microstructure containing a 35 particles with two P_0's, namely 0.003 and 0.0217. The coefficient of variation as presented in Table 2b is below 0.011. This value is an indication for the intrinsic variation of the CEMHYD3D model. The variation of a single particle size within all models is comparable to this intrinsic variation and therefore this variation is intrinsic to the chosen simulation method (e.g. cellular automata).

Table 2 (a) Statistical information on the derived values of β for d = 7, 13, 21, 25 and 35 and $P_0 = 0.003–0.099$ in the constant particle size case, (b) statistical information on derived values of β for 10 simulations with d = 35 and $P_0 = 0.003$ and d = 35 and $P_0 = 0.021$

	β
(a)	
Mean	4.817
Median	4.800
SD	0.094
Variation	0.009
Coefficient of variation	0.020

	$P_0 = 0.003$	$P_0 = 0.0217$
(b)		
Mean	4.741	4.732
Median	4.725	4.734
SD	0.053	0.040
Variation	0.003	0.002
Coefficient of variation	0.011	0.009

Fig. 5 shows the surface area of the (shrinking) core during the reaction compared to the theoretical surface area as derived in [12]. One can notice that the surface area of simulation is slightly higher than the theoretical curve, and that the difference between the curves is comparable to [12].

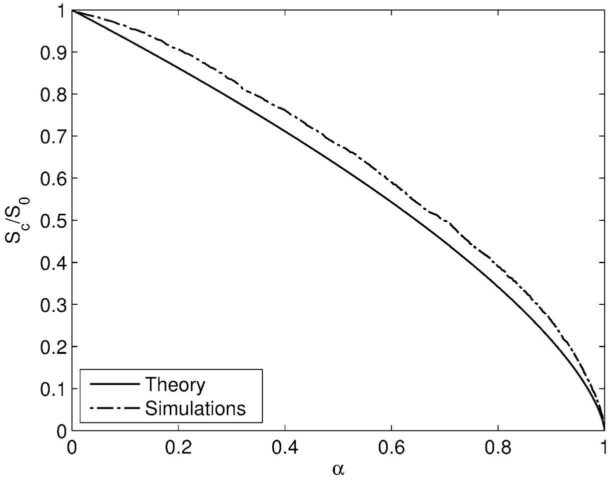


Fig. 5 The surface area of the shrinking core during reaction in CEMHYD3D compared to the theoretical surface according to the ash diffusion controlled model of Levenspiel [13], given as Eq. 9 in [12]

Varying particle size case

In the previous section, a system with v = 1 was evaluated. In this case, the reactant has transformed into the product without any change in the volume of the solid during the process. In practice, often a change in volume during reaction occurs ($v \neq 1$). In this section, a system with v = 1.7 is used as an example, which means that the volume of the product ($V_e - V_c$) is 1.7 times the reacted volume of the reactant ($V_0 - V_c$) (Fig. 1). In order to cope with this volume change within CEMHYD3D, a modification was needed. In the original version of CEMHYD3D of Bentz [36], the additional product formed during the reaction was randomly distributed through the microstructure, although with a slight favor for placing in contact with a solid. Fig. 6 shows the reaction of a 35 particle including the formation of additional product. One can notice from Fig. 6 that some voxels appear

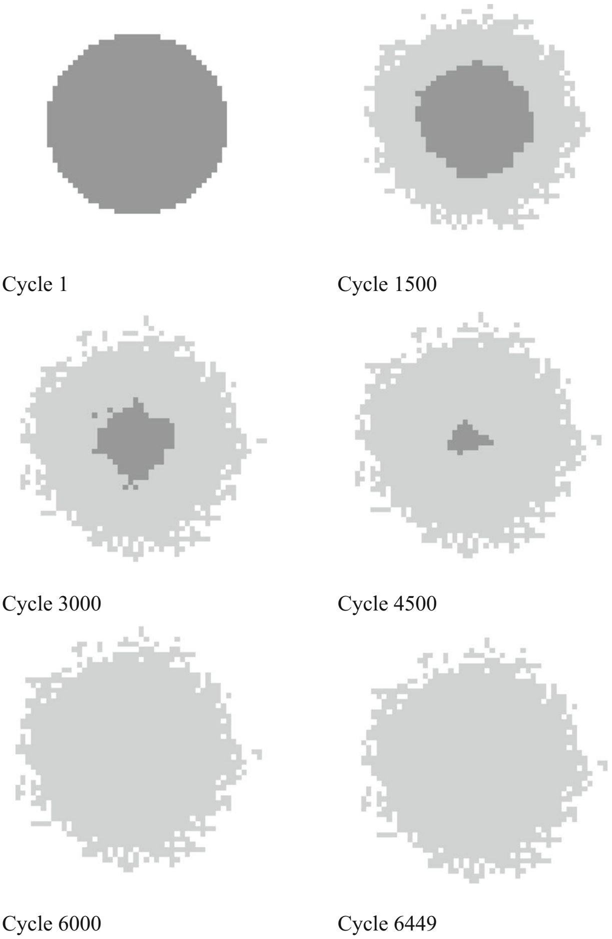


Fig. 6 Example of dissoluting particle and the developing shape during its reaction in case of v = 1.7 (in red the unreacted core and in blue the formed reaction product)

Table 3 (a) Statistical information on the derived values of β for $d = 7$, 13, 21, 25 and 35 and $P_0 = 0.003$–0.099 in the varying particle size case, (b) statistical information on derived values of β for 10 simulations with $d = 35$ and $P_0 = 0.003$ and $d = 35$ and $P_0 = 0.021$

	β
(a)	
Mean	5.171
Median	5.175
SD	0.079
Variation	0.006
Coefficient of variation	0.015

	$P_0 = 0.003$	$P_0 = 0.217$
(b)		
Mean	5.121	5.170
Median	5.121	5.171
SD	0.051	0.046
Variation	0.003	0.002
Coefficient of variation	0.010	0.009

to be unconnected to the core, but in fact they are connected to the particle. This appearance of loose voxels is caused by the chosen representation which is cut-through with a thickness of only 1 voxel.

For the testing of the general reaction equations, it is necessary that the additional product voxels are placed on the surface of the 'digitized sphere'. Therefore, a routine is added, which searches a spot on the surface suitable placement/precipitation of this additional product voxel. Fig. 6 shows the slice through of a dissolving particle, with the unreacted core in red and the formed reaction product in blue. One can notice that the spherical shape of the reactant and the hydration product is maintained during the reaction.

Analogously to the analysis in the previous section, the current section deals with the analysis of the varying particle size case ($v = 1.7$). The particles in these systems grow due to the fact that more volume of product is formed than the volume of reactant that is disappeared.

Table 3a shows the results of the model with a single relation constant β_2 for 132 simulation runs (with each curve the $R^2 \geq 0.994$). It can be noticed from this table that the coefficient of variation is around 1.5%. The coefficient of variation, when performing ten simulations with the same initial microstructure is around 1.0% (Table 3b). This value has been determined by determining the β_2-value for 10 simulations starting with the same initial microstructure.

Table 4 and Fig. 7 show the results of the same analysis for more ash/reactant ratios (v). As one can notice from Fig. 7, β_2 slightly depends on v. Based on the present theory, a constant value for β_2 would be expected. Nevertheless, the deviation of β_2 is 10.7% for the relevant range of v between 1 and 2.5, so with mean $\beta_2 = 5.1$ the maximum error is about 5%. Larger values of v are hardly found in

Table 4 The derived values of β_2 for different values of the volume increase ratio v in the diffusion controlled phase

v	β_2
1	4.817
1.05	4.848
1.35	5.018
1.7	5.171
2.5	5.360
3.4	5.480
4.25	5.552
5.1	5.585
5.95	5.627
6.8	5.638

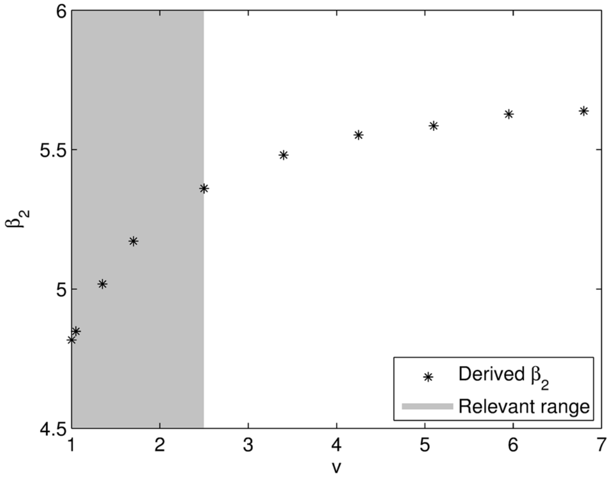


Fig. 7 A graphical representation of the derived values of β_2 for different values of v in the diffusion controlled phase and marked area representing the relevant range of v for the reaction of the four main cement clinker phases with water

practice. For cement reactions, for instance, the minimum and maximum volume expansions of the reaction of the four (main) cement clinkers phases with water are 1.69 and 2.27.

Coupling cellular automata and reaction kinetics

"Constant particle size" and "Varying particle size case" sections presented the relation between cycles and the theoretical model from the transition point onwards. In this section, a relation between time and cycles is derived. Before the transition point, the relation only depends on the chemical reaction model and the relation is equal to the unique relation derived in the previous paper [12]. From the transition point onwards, it can be assumed that the reaction time is the summation of the time needed to reach the transition point using the chemical reaction controlled model and time needed to reach a certain reaction degree from the transition point onwards.

The time to reach a certain α during the diffusion controlled phase from the transition point (t_{tr}) onwards can be calculated using Eq. 17. Analogously to [12] instead of time, this point can also be described based on cycles and reads;

$$(C - C_{tr})\frac{k_2}{r_0^2} = -\frac{(v + (1 - v)(1 - \alpha))^{2/3}}{v - 1} - (1 - \alpha)^{2/3} + \frac{(v + (1 - v)(1 - \alpha_{tr}))^{2/3}}{v - 1} + (1 - \alpha_{tr})^{2/3}. \tag{27}$$

Based on this the following relation for the diffusion controlled phase can be derived

$$t - t_{tr} = \beta_2 (C - C_{tr})\frac{P_0}{k_2}\frac{r_0^2}{r_p^2}. \tag{28}$$

Here β_2 is the fitting parameter for the diffusion controlled phase. The time needed to reach the transition point (t_{tr}) according to [12] and for $C = C_{tr}$ is:

$$t_{tr} = \beta_1 (C_{tr} - 2)\frac{P_0}{k_1}\frac{r_0}{r_p} \tag{29}$$

Combining Eqs. 28 and 29, the total time becomes:

$$t = \beta_1 (C_{tr} - 2)\frac{P_0}{k_1}\frac{r_0}{r_p} + \beta_2 (C - C_{tr})\frac{P_0}{k_2}\frac{r_0^2}{r_p^2}. \tag{30}$$

Here β_1 and β_2 are the relation constants for the chemical reaction controlled and diffusion controlled systems, k_1 and k_2 are the kinetic parameters of the chemical reaction controlled and diffusion controlled systems, respectively, r_p is the radius of the particle in voxels, r_0 is the initial size of a reacting particle and P_0 is the reaction probability according to cellular automata model.

Similarly to [12], a unique relation (Eq. 30) is established here between cellular automata (r_p, C, P_0) and chemical kinetic (r_0, t, k_1 k_2) properties using the relation constants β_1 and β_2 for chemical reaction controlled and diffusion controlled reactions, respectively. This enables the direct coupling of the cycles from the cellular automata model to time, which is basis for the description of reaction in the general chemical kinetic models. During the current research β_1 of 1.31 was found for $v \geq 1$ and a value of 5.09 with deviation of 5% can be applied for β_2 in the relevant v range of 1–2.5.

Conclusions

Cellular automata is a powerful technique to model chemical reactions/systems [1–9, 12, 14], providing it with the ability to simulated comprehensive chemical reactions. As pointed out by Kar et al. [41], cellular automata is a stochastic approach in which a natural event can be successfully simulated. Cellular automata leads to an accurate mathematical model which can clarify the role of individual components within processes and generate specific, testable hypotheses and predictions. To be able to do this, cellular automata assumes that time and space are discrete. Therefore the challenge with cellular automata systems is to establish a direct link between time and cycles, which is the 'time-based' parameter in cellular automata. Often a square root between cycles and time is used. This approach is also used by Bentz [36], based on the Knudsen Approach [42]. This challenge was addressed by Van der Weeën et al. [4] by presuming a time step of 0.01 s, when coupling a cellular automata model to a partial differential equations based model.

This paper intends to provide a unique direct relation between time and cycles for diffusion controlled systems as earlier done for surface controlled reactions [12], rather than the general approach given by Knudsen. This is of interest, since in many reactions a layer of reaction products is formed on the unreacted core, rendering the reaction diffusion rather than surface controlled. The studied system starts as a surface controlled system, which is inherent for the cellular automata approach, until a certain reaction product layer thickness is reached. From this point of time, the diffusion controlled mechanism can be the rate determining reaction mechanism.

The cellular automata approach is applied to different ash layer models for particles with constant ($v = 1$) and growing/shrinking ($v \neq 1$) particle sizes. Simulations are performed for particle sizes 13, 21, 25 and 35 and reaction probabilities ranging from 0.003 to 0.099 with a step of 0.003. It is shown, from the results of these simulations, that the cellular automata approach can adequately describe both cases for a reaction degree larger than the transfer reaction degree (α_{tr}) using diffusion (ash layer) controlled model. The threshold reaction degree is the reaction degree at which a diffusion layer of 1 voxel is formed. A hybrid reaction model based on chemical reaction controlled and (ash) diffusion controlled model has been introduced in order to address the existence of the transition reaction degree.

Here, the cellular automata parameters are mathematically related to the kinetic parameters of the CRC and ash diffusion model, for which two general constants, β_1 and β_2, respectively, are introduced. This is achieved by computing the mathematical relation between the cellular automata simulations and the chemical reaction models for 132 different simulations with varying particle sizes and reaction probabilities. A value of 1.31 was found for the relation constant β_1, while a relation between the product/reactant ratio v and the relation constant (β_2) is found for $v \geq 1$ from threshold reaction degree onwards. The coefficient of variation for 132 simulations is around 2%. It should be noticed that typical cellular automata simulations have already an intrinsic coefficient of variation of 1% owing to their statistical nature, since it depends on probabilities for transitions. Furthermore, for the relevant range of v, an average β_2-value of 5.09 can be applied. The minimum and maximum value are respectively minus and plus 5%.

This relation is tested from the threshold reaction degree α_{tr} (so the transition point between chemical reaction and diffusion controlled) onwards. Since the full conversion time is of interest, a hybrid model is introduced here, which combines the chemical reaction controlled and diffusion controlled phase. Using this hybrid model, a unique relation between time and cycles based on the parameters of cellular automata (particle size and reaction probability) and chemical models can be derived (Eq. 30).

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