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SPACE system for simulation of aggregated matter application to cement hydration

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Abstract

This paper presents the basic features of the Software Package for the Assessment of Compositional Evolution (SPACE). SPACE consists of a two-stage simulation strategy, providing successively for the three-dimensional packing of a particulate system and the structural evolution, the latter representing a sintering, foaming, or hydrating particulate system. Hence, SPACE has versatile potentialities. The initial distribution results from a generation process in which a predefined number of particles are dynamically mixed using a Newtonian motion model. Bulk material and interfaces can be simulated. The results obtained have been demonstrated to be realistic. Next, this paper deals with the simulation of cement hydration as an illustrative application of the SPACE system. The model starts with a simulated spatial distribution of anhydrous cement particles in a water-filled volume and simulates the hydration process through a series of relatively simple growth rules, which are iterated many times. The kinetic hydration model used here is similar to one used by van Breugel. The chemical reaction between cement and water results in expansion of the particle and in the formation of multiple contacts with other hydrating particles. The effects of this interparticle contact as well as the effect of water consumption on the hydration and expansion rate have been explicitly accounted for, with the aid of a surface sampling method that can efficiently evaluate the degree of contact between particles. Results from various numerical experiments will show the microstructural development in bulk and in the interfacial zone.

Keywords: Hydration; Kinetics; Interfacial transition zone; Microstructure; Particle size distribution

1. Introduction

The interest in particle packing arises in different areas in engineering. This interest can be explained in that a large proportion of natural and manufactured materials we deal with are, or contain, aggregates of several shapes and sizes. “Particles” are conceived in these fields as aggregate grains, minerals, metal or chemical powders, soils, molecules, pores, or rocks. The behaviour of such materials depends partly on the properties of the composing parts of the material body and partly on their interaction pattern. Some composite properties are structure insensitive, but most properties are structure sensitive, thereby reflecting the underlying internal particulate structure.

For example, in concrete, damage evolution as observed at a mesoscale is governed to a large extent by the granular aggregate structure. It is generally accepted that the zone around aggregates in the cementitious matrix is the weakest in the mechanical system. Because the aggregate constitutes a dense random packing, it yields as a consequence a dense network of weak interfaces. Obviously, loading the material body results in a cracking behaviour that is governed by the aggregate skeleton.

At the same time, on a microscale, fresh cement paste can be considered a granular mixture of cement particles in water. Evaluation of the cement structure and hydration process in the interfacial zone (ITZ) around aggregates can lead to an improved understanding of the material behaviour, not only at a microlevel but on higher levels as well. For opaque materials such as concrete, it would require some effort to acquire this sort of structural information in an experimental way, such as by using microtomography [1].

The approach that aims to simulate the hydration of cement paste is presented in this paper. A model is introduced that simulates the granular structure of fresh cement at the microlevel as a spatial distribution of spherical (cement) particles diluted in an aqueous matrix. An iterative algorithm simulates the mixing process of the ingredients by specifying the mechanical behaviour of each element when contact occurs with other objects and by relating the element’s dynamic behaviour with respect to external forces. Until a desired distribution has been obtained the elements are presumed chemically inactive. When the hydration pro-

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cess starts, the elements become chemically active but remain spatially fixed. During this process, the chemical composition and corresponding spatial geometry of the particles change iteratively based on a preimposed kinematic model. Eventually, the interaction between simultaneously expanding particles determines the local and global behaviour of the cement paste. The paper will present some numerical experiments illustrating the microstructural evolution of cement hardening in bulk and at the interface.

2. Material representation

To describe the nonhomogeneous granular nature of the internal material structure, the model assumes the material is composed of a finite number of discrete elements. Each element represents by its shape and size a characteristic phase in the material. These elements are dispersed in a presumably homogeneous and uniform matrix and are spatially restricted by a cuboidal volume. To study interface effects the volume boundary can be given rigid properties, whereas periodic boundaries are used to simulate bulk space. In doing so, cement paste is modelled as a mixture of spherical cement particles dispersed in an aqueous matrix. Aggregate grains are considered much larger so that their influence on local cement particle packing can be assumed similar to that of a plane surface (rigid container wall). For such a model to have any realistic value, the distribution of particles (of macro-, meso-, or microsize) should reflect (at least) the following phenomena:

- Mutual particle influence: especially at higher densities or when particles differ considerably in shape, mechanical contact between particles play a dominant role on the mutual spatial distribution
- Wide range of particle densities: for concrete aggregates up to maximum density, and for cement particles volume densities associated with values of w/c between 0.13 and 0.6
- Formation of interface zones near rigid boundaries: distribution characteristics of particles (either aggregate near the mould or cement particles near aggregate grains) in the vicinity of rigid interfaces differ significantly from that in bulk space.

A commonly used method to randomly distribute particles in a limited volume places particles one after the other (sequentially) at random locations, taking care not to overlap other particles or the boundary [2]. In these processes, the spatial positions of successfully placed particles are not influenced by the particles added later. For example, to simulate the behaviour of larger particles pushing smaller particles aside, it is necessary to place the particles in order of decreasing size. This method aims to imitate the observed static granular structure by direct generation. Nevertheless, when analyzing a material specimen, we essentially observe the result of a dynamic process in which a large number of influences determine the final structure.

Seeing it from the perspective of a single element, it will undergo influences from all sources in finding its destination (position, orientation) inside the container during the production/generation process. It is the internal influence of "particle" interference (i.e., chemical, physical, or mechanical interaction), and the external influences such as the container walls, gravity forces, and "particle"-matrix friction that determine the final distribution of the particles.

3. Mixing process

It seems more natural to generate the particle packing indirectly by simulation of the dynamic mixing process. The general concept can be described as follows. Information about the ingredients, such as shape, size, mass, and volume density, have to be provided by the user, whereupon an initial distribution is created by a sequential assigning process similar to the one described. Except for the "nonoverlap" restriction, none of the other conditions has yet influenced the distribution. It has been shown that only a limited maximum density can be reached by such processes using monosized particles [3]. In practice, density can be increased by enlarging the width of a multisized particle distribution, but maximum packing densities cannot be obtained under normal conditions. Therefore, the densification as described later may be necessary.

Next, the actual dynamic mixing process commences and the elements are iteratively moved to new geometrical positions according to a model that describes the most likely change of the particle's spatial position and geometrical orientation with respect to its "environment." Herein the "environment" of a particle consists of neighbouring particles, container walls, and other influences that act on the particle. By temporarily freezing all other elements the trajectory of the active element is checked for interelement contact. The object is displaced for one time step or up to its first contact. Velocities of the objects immediately after contact are calculated by a contact model and are assigned to the objects, whereupon the next contact is searched within the remaining time. The process continues until a desired (stable) configuration is obtained. High fractional density values are achieved by gradual decrease of the container size during the mixing process. Due to the spatial constraint of the container, densification is either caused by mechanical contact with periodic neighbours or by mechanical contact with the rigid boundary of the container. The latter results in a disturbance in the packing near the specimen boundary. A more elaborate description of the mixing process is given in Stroeven and Stroeven [4].

4. Hydration process

From here on, the obtained particle distribution becomes chemically active. The now stationary cement particles will react with water to form so-called gel products. Here, too, the hydration behaviour of each element with respect to its "environment" is specified rather than the behaviour of the entire mixture. The development of interelement contact between simultaneously hydrating particles will characterize the hydration behaviour of the material.

It should be mentioned that due to our interest in the structural development of the cement paste, the chemical reaction between the constituents is expressed in volumetric changes. The hydration process will be outlined in two steps. First, representation of a hydrating cement particle as a set of concentric spheres will be clarified based on the hydration description of a single particle. Second, the interaction mechanism between the various particles will be studied.

4.1. Step 1: hydration of a single cement particle

The kinetic hydration model used here to describe the hydration behaviour of a single particle consists of two subsequent stages [5,6]. The first stage, in which a phase boundary mechanism controls the hydration rate, is followed by a stage in which the reaction rate is controlled by a diffusion mechanism. The transition between the two stages is assumed to occur when the thickness of the layer of reaction product $d(t)$, precipitated on the cement particle at time t, equals a transition thickness δ_{tr}. The inward growth or decrease of the unhydrated cement surface Δr_{in} for a sufficiently small time period Δt is then given by Eq. (1) [5]:

$$\Delta r_{\text{in}} = \Delta t K_0 \left(\left(\frac{\delta_{\text{tr}}}{d(t)}\right)^{\beta}\right)^{\lambda} \qquad \begin{array}{l} \lambda = 0 \ \ \delta_{\text{tr}} > d(t) \\ \lambda = 1 \text{ otherwise} \end{array} \tag{1}$$

where K_0 is the rate constant (in μm/h) and constant β regulates the diffusion process. The chemical reaction between cement and water results in a gel product. The relationship between the volume change ΔV_{in} of the hydrated cement and the volume change ΔV_{out} of the gel or outer product is given by Eq. (2):

$$\Delta V_{\text{out}} = v_1 \Delta V_{\text{in}} \tag{2}$$

where constant $v_1 = 2.2$ [5]. A volume of ΔV_{in} of the reaction product is used to fill the space of the reacted cement. The remaining volume precipitates equally on the available surface of the existing gel, thereby introducing an outward growth. In this simulation the amount of water that is chemically or physically bound to the cement is taken a fraction $v_2 = 0.4$ by weight of the reacted cement [5]. Consequently, a reacted volume of ΔV_{in} cement requires a volume of water as given in Eq. (3):

$$\Delta V_{\text{water}} = v_2 \rho_c \Delta V_{\text{in}} \tag{3}$$

where $\rho_c = 3.15$ (g/cm^3) represents the volumetric density of cement. The values for v_1 and v_2 have been proposed by van Breugel [5] and are based on experimental observations. Due to the discrepancy between the volume of the reaction product and the total volume of reacted cement and water, a fourth phase, air, is introduced. The reduction of the water supply occurs at the air-water interface, which results in an outward growth of the air layer.

A uniform deposition of the gel product onto the available gel surface, a uniform decrease of the entire cement surface, and a uniform consumption of water from the available water-air surface is assumed. Subsequently, the cement-gel interface as well as the gel-air and air-water interfaces remain located on concentric spheres throughout the hydration process (Fig. 1A). This is particularly convenient for modelling purposes. The product thickness $d(t)$ in Eq. (1) is thus given by $r_{out} - r_{in}$. It should be noted that the formation of an air layer around the gel in the model is merely used to accommodate for the local consumption of water. It is not intended to represent the actual location of air. It is assumed that if water is still available for a particular particle (i.e., there exists an air-water interface for that particle), it will be equally available for the entire cement surface, hence causing a concentric decrease of the cement core.

4.2. Step 2: interaction between multiple hydrating cement particles

The simultaneous expansion of multiple neighbouring particles and the limited amount of available water will sig-

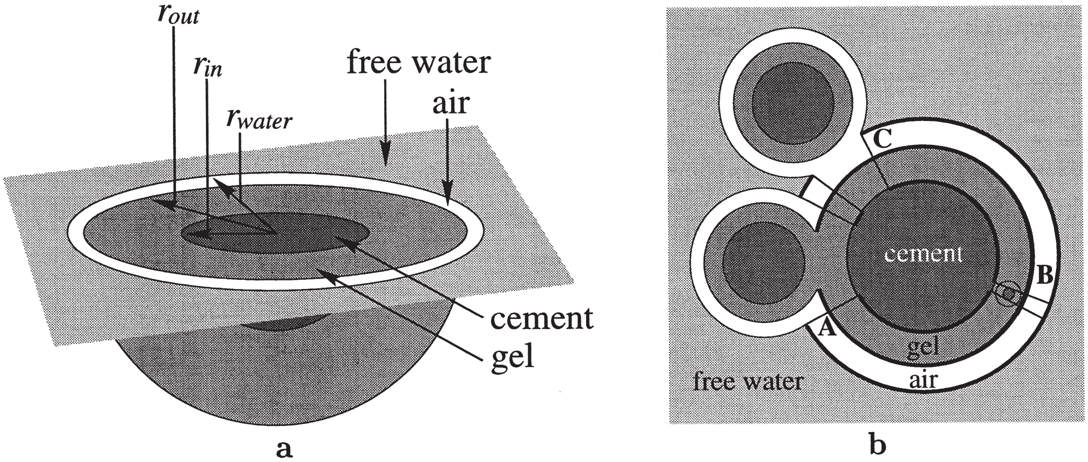

Fig. 1. (a) Geometrical representation of hydrated cement and (b) various contact situations between cement particles.

nificantly affect the hydration behaviour of a single particle. First, growing contact areas between the gel products of neighbouring particles diminishes the surface area that is available for product deposition. A two-dimensional representation of this situation where the thick line at the gel-air interface represents the free surface onto which the gel product may precipitate is shown in Fig. 1B, case A. Less surface area signifies a thicker deposit of the product layer. Second, the consumption of water can only occur at the interface between air and free water (represented in Fig. 1B by the thick line at the air-water interface). Finally, mutual contact and water shortage influences the inward growth of the cement. For example, the particle embedded in the gel layer as illustrated in Fig. 1B, case B, prevents part of the gel surface from being active in the hydration process (shielding) and the reduction of free water in (Fig. 1B, case C) diminishes the inward growth even more.

Let $A_{\mathrm{water}}(t)$ be the surface area of the air-water interface of a particle at time t and let $A_{\mathrm{out}}(t)$ correspond to its gel-air interface surface. The factor $\omega_1(t)$ in which the shielding effect and the water reduction are included represents the fraction of the cement-core surface that is active in the hydration process at that time.

Note from Fig. 1B that the evaluation of $A_{\mathrm{water}}(t)$, $A_{\mathrm{out}}(t)$, and $\omega_1(t)$ requires the determination of nonintersecting or free surface between multiple fused spheres. Although an exact solution to this problem exists [7], it involves an elaborate number of calculations, especially when more than two spheres mutually intersect. To efficiently evaluate the free surface of a sphere, an algorithm has been implemented that divides the surface in triangular tesserae, or surface patches (illustrated in Fig. 2A) of which only the center of each patch is stored [8]. Each patch is assigned "free" if its center is not contained by any other intersecting sphere. The values of $A_{\mathrm{water}}(t)$ and $A_{\mathrm{out}}(t)$ can now be determined. As an example, Fig. 2A indicates the detected surface patches onto which the gel product can be deposited.

The correction factor ω_1 is determined in two steps. First, the total number of cement-core patches active in the hydration process is taken equal to the number of free water-air surface patches. This accommodates for the water reduction (Fig. 1b, cases A and C) effect.

Second, it is determined whether the corresponding point on the gel-air surface of each remaining free surface point had been inactive during an earlier hydration stage. If so, they are considered inactive too. This operation imitates the shielding effect of particles that are partly embedded in the gel (Fig. 1B, case B).

To conclude, an iterative repetition of the following procedure implements the hydration process:

1. Determine Δr_{in} according to Eq. (1). Calculate the volume change ΔV_{in} when only a fraction ω_1 of the cement surface hydrates. Calculate a new value for the inward growth $\Delta r'_{\mathrm{in}}$ when a concentric decrease is assumed.
2. Determine ΔV_{out} using Eq. (2) and calculate the outward growth when precipitation only occurs on the surface A_{out} (illustrated in Fig. 2B)
3. Determine $\Delta V_{\mathrm{water}}$ using the relationship in Eq. (3) and calculate $\Delta r_{\mathrm{water}}$ when water is only consumed from the surface area A_{water}.

Visual and numerical evaluation of the structure after every time step provides insight into the dynamical behaviour of the cement paste. Examples will be shown next.

5. Experiments and evaluation

For experimental purposes, six different spatial distributions were generated representing the (unhydrated) cement

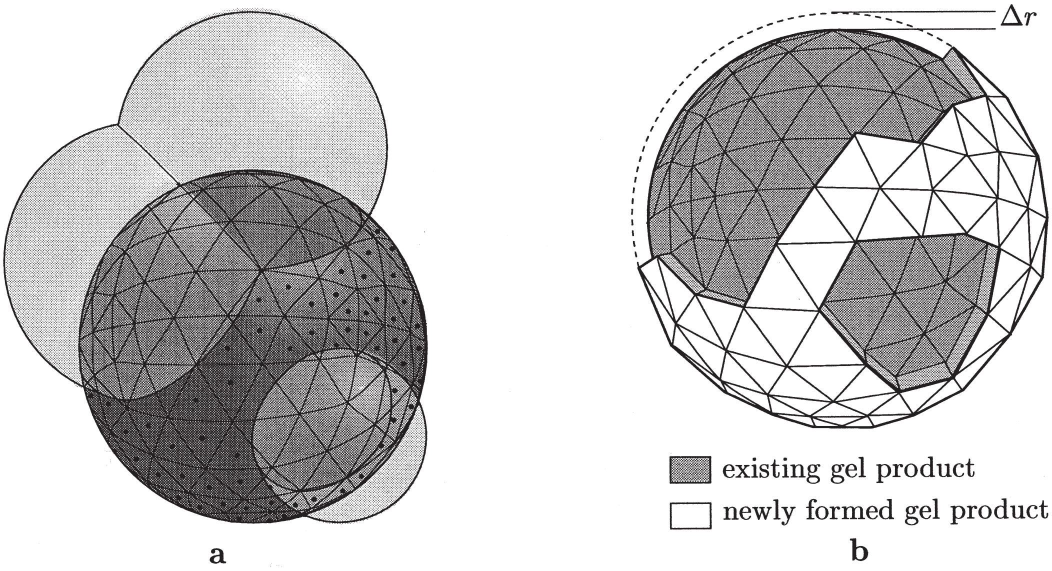

Fig. 2. Coarse tessellation of sphere surface. (a) Detected free surface area for product deposit (indicated by dotted patches). (b) Estimated radius increase Δr.

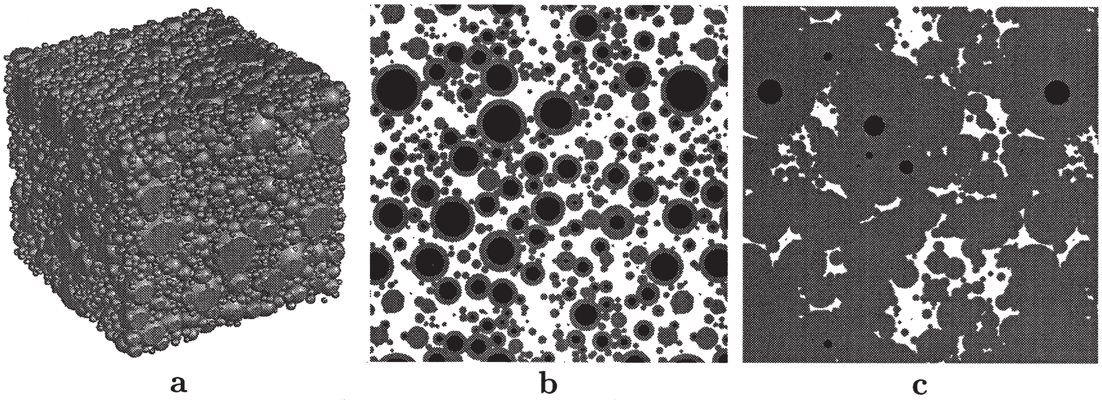

Fig. 3. (a) Three-dimensional view of hydrated cement paste and structure development as observed in a section plane after (b) 3.2 days and (c) 10 years of hydration. White areas indicate water + air, gray areas represent gel, and black areas correspond to unhydrated cement.

paste. Three specimens simulate the particle packing in bulk material, each with a different value of w/c (0.50, 0.39, 0.42, 0.26), and with the same three values of w/c the remaining specimens are generated simulating fresh cement near a rigid aggregate surface. All six specimens originate from a single initial distribution of 10,000 elements with size distribution according to the Rosin-Rammler function with $n = 0.98$, $b = 0.038$, and Blaine surface = 355 [5]. The maximum and minimum diameter were taken as 15 and 1.5 μm, respectively. The various w/c ratios were obtained by mixing and densification of the initial distribution. For bulk material the boundaries are taken to be periodic to avoid influence of the container on the particle packing. In contrast, rigid boundaries are assumed to enforce local disturbance in the particle packing. All specimens were hydrated with identical parameter settings ($K_0 = 0.01$ μm/h, $\delta_{tr} = 2$ μm, and $\beta = 1.0$) for a period of several simulated years. As an illustration of the structure development, Fig. 3A shows a three-dimensional view of the specimen with w/c = 0.26 and rigid boundaries after full hydration. The illustrations in Figs. 3B and 3C show the various chemical phases that can be observed at a section plane after a hydration period of 3.2 days and 10 years, respectively (w/c = 0.50, periodic boundaries). The effect of particle embedding and local shortage of water are reflected in that even, after a period of 10 years, some of the (larger) particles are not completely hydrated.

5.1. Experiment 1: mechanical strength vs. hydration degree

To compare the mechanical behaviour of the simulated cement paste with experimental findings, it is assumed that strength development in hydrating cement paste is primarily governed by the amount of particle contact. For this purpose the total contact area between mutually intersecting particles per unit of volume has been determined after every time step during the hydration of all three "bulk" specimens. The result is shown in Fig. 4A by the thick line as a function of the degree of hydration (fraction of hydrated cement with respect to the initial cement volume) for three values of w/c. They can be compared (taking the ultimate strength of w/c = 0.5 as a reference) with the strength development as proposed by Locher in reference [9] indicated by the dashed lines in Fig. 4A.

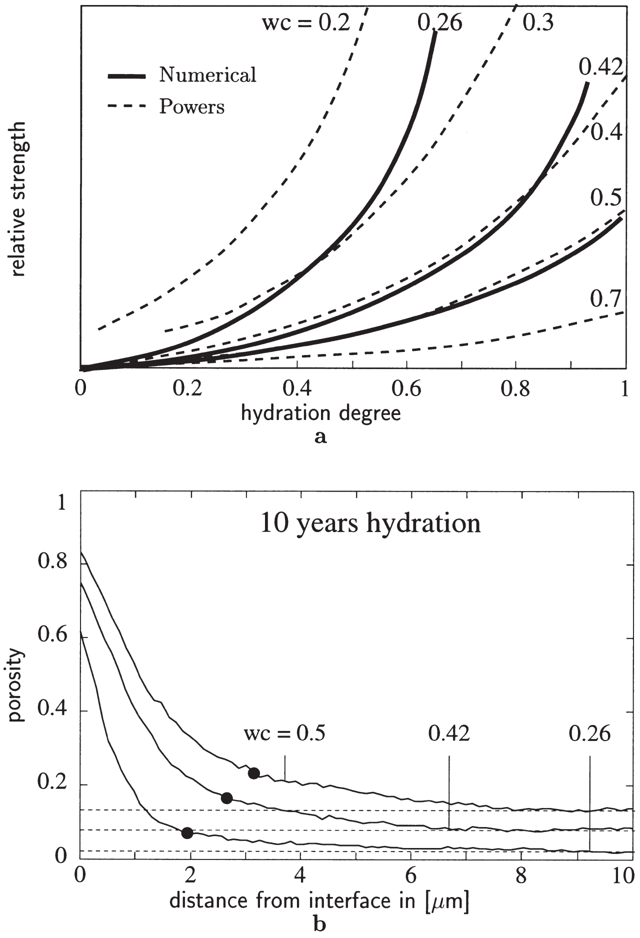

Fig. 4. (a) Estimated relative strength as a function of the hydration degree vs. proposed curves by Locher [9] and (b) porosity variation near the interface for three different w/c ratios.

Obviously, the strength of a cement paste cannot be predicted exactly by volumetric particle contact only. Even so, a relatively accurate estimate of the strength development is reflected by the model for all three w/c ratios.

5.2. Experiment 2: influence of w/c on the thickness of the ITZ

It is not intended here to measure the exact thickness of the ITZ but merely to observe the influence of w/c on the ITZ. For this purpose, local porosity is assumed to be related to the micro (mechanical) behaviour of the material (the higher the porosity, the lower the microhardness). The curves in Fig. 4B show along the y axis the local porosity measured on a section plane parallel to one of the boundaries (interfaces) of the cube as a function of the distance between the plane and interface. The porosity was determined using a random point sampling method. Clearly visible is the large porosity peak close to the (aggregate) surface, which results because the particles cannot be packed properly close to a boundary. The porosity values in bulk material are indicated by the dashed lines for each value of w/c. A dot indicates the border of the ITZ where porosity is “approximately” equal to bulk value. This is arbitrarily chosen at a drop of 80% of the difference between porosity at the boundary and in bulk. The shift in location of the points indicates a decreasing thickness of the ITZ for a decreasing w/c ratio, a tendency that is generally acknowledged [10].

To conclude, the relative simple model in which physical, chemical, or mechanical laws determine the behaviour of a single particle and interparticle relationships determine the overall behaviour of the mixture offers a variety of applications of which cement hydration is only one. The potentialities of SPACE—allowing simulatation of “particle” packings based on an arbitrary size distribution and of arbitrary density up to the maximum one—should be compared to those of other available approaches in the various fields to which the present system can be applied. “Particles” can be void, of course, representing pores or bubbles in a foam system. It should be noted that in validating SPACE estimates in the various application domains, the researcher has two degrees of freedom in controlling the energy dissipation by particle collision and/or by friction between particles and the “matrix.” Hence, in addition to mainstream possibilities for simulating arbitrary intermediate states between randomness and order in the full range between low and maximum densities, the latter facility allows the possibility to change from uniform to clustered (flocculated) systems.

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