COMPUTER SIMULATION STUDY OF CONCRETE’S SELF-HEALING CAPACITY DUE TO UNHYDRATED CEMENT NUCLEI IN INTERFACIAL TRANSITION ZONES

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Nuclei of cement particles left unhydrated in concrete after maturation can provide under favorable conditions self-healing capability to micro-cracked concrete. A prerequisite is of course that the small cracks for which repair by self-healing is considered pass through regions containing the unhydrated cement. Such micro-cracks predominantly run through ITZs. Therefore, containers with rigid boundaries were employed for the production of series of cement pastes by a concurrent algorithm-based computer simulation system with the acronym SPACE. They were subjected to quantitative microstructure analysis of which the data on relevant gradient structures in the ITZ are presented and discussed in this paper in terms of concrete’s possible self-healing capability.

Keywords: computer simulation, self-healing, unhydrated cement nuclei

1 Introduction

Shrinkage and local secondary displacements during maturation lead in the virgin state to the formation of myriads of tiny cracks in the concrete’s cement paste, the major part of which will be situated in interphase regions around aggregate grains [1]. Additional micro-cracks can be initiated, of course, by external influences, such as by freeze thawing, temperature gradients and mechanical loading. The dispersion of such cracks is inevitably governed by the dispersion of the aggregate grains in the so-called jammed state. These fine cracks can heal under favorable conditions, a phenomenon referred to at least as early as 1937 by Turner as self-healing [2] or autogenously healing. Several mechanisms of self-healing are proposed [3], i.e., hydration of the hitherto unhydrated cement, formation of insoluble calcium carbonate, and mechanical blocking by very fine material suspended in the water.

This paper focuses on the first mechanism in a computer simulation approach, whereby the self-healing capability can be expected primarily depending on the amount of unhydrated cement. However, also number density and spacing distribution of unhydrated cement nuclei (UCN) could play a role, defining it as a configuration-sensitive phenomenon [1]. The problem that should be tackled concerns the assessment of the (near) intersection frequency of dispersed micro-cracks and dispersed unhydrated cement particles. This would require a complicated multi-scale modelling approach. This paper will only consider properly simulating the spatial UCN structure.
To do so, the simulation system must be capable of dispersing the cement particles “realistically” in the fresh state. This can be achieved only by the Delft-produced concurrent algorithm-based SPACE system [4,5].

Concrete is a macroscopically heterogeneous material, requiring elements of macroscopic dimensions to reduce scatter to an acceptable level in the various independent global descriptors of its structure. Such elements define the size of the “homogeneous” representative volume elements (RVEs) for successive descriptors. Order of magnitude of the linear dimension of a cube-shaped RVE for composition homogeneity is about four times the maximum grain size [6]. However, the same linear dimension may be an order of magnitude larger when dealing with extreme configuration-sensitivity [1,7]. The average nearest neighbor aggregate grain surface-to-surface spacing in normal concrete is of the order of 50μm [8], in a range of 0.1~200μm [9]. Pocketed between two or more aggregate grains, major part of the cement paste will therefore be inside ITZs with basically properties deviating from those in bulk. Density is lower, and porosity and connected fraction of porosity are found concentrated inside ITZs [13-15]. The relevance of focusing on the ITZ in this paper is therefore coming from the high probability that a crack will traverse this zone [18].

Experimental information seems limited to self-healing effects in concrete elements provided with a single relatively small crack subjected to mechanical loading [12,13]. Further, only scare experimental evidence is available as to technological influences (such as water to cement ratio and cement fineness) on the self-healing capacity of concrete [14].

2 Materials

Three different types of Portland cement (PC) are employed in pastes with water to cement ratios (w/c) of 0.2, 0.3, 0.4, 0.5, and 0.6. The PC types are denoted by C206, C319, and C497, whereby the Blaine number defines the specific surface area in m²/kg (i.e., C206 is a cement with Blaine number 206). The respective particle size distribution (PSD) functions comply with the so-called Rosin-Rammler size distribution function [4,15,16]

\[ G(d) = 1 - \exp(-bd^a) \]  

in which a and b are two constants that have to be specified for each cement type and d is sieve size. The cumulative size distribution curves of the model cements are shown in the Fig. 1, with grain sizes between 1 and 34.7μm, 1 and 26.2μm, and 1 and 18.8μm for C206, C319 and C497, respectively.

Figure 1: Cumulative PSD curves for the cements used in the simulation study
3 Methodology

The discrete element simulation system SPACE models the fresh paste as a set of spherical elements dispersed in water. Since these elements represent real physical phases in the material, physical properties can be assigned to each element along with its size. There are two vital stages incorporated in the SPACE system [17]. A dilute 3-D distribution of elements with pre-defined size distribution is generated in the initial stage in a container. Next, random linear and rotational velocity vectors are assigned to each element. Then during dynamic packing mixing, the location and orientation of all particles are changed at each time step according to a Newtonian motion model. Finally, the iteration stops when a certain condition is met, e.g., the relevant volume fraction of particles is reached. Another vital stage is the hydration process. Individual hydrating cement particles are represented by sets of concentric spheres in the early stages of the hydration process. The kinetics of the hydration process is governed in an initial stage by a boundary mechanism, followed by one in which the reaction rate is controlled by a diffusion mechanism. For more detailed information, see Stroeven [4, 17]. The hydration algorithms largely correspond to those of van Breugel [16].

4 Experimental

For each specimen, a total number of 5000 cement particles were generated conforming to the three PSDs of Fig.1. After dynamic packing, model cements with final volume fractions of 35%, 39%, 44%, 51% and 61% were obtained, corresponding to w/c ratios of 0.6, 0.5, 0.4, 0.3, and 0.2, respectively. Each combination of parameters was represented in this preliminary study by a single cube. The final linear dimensions of the cubes were in the range 75.7–91.1, 51.3–61.7 and 40.7–49μm for C206, C319 and C497, respectively. Hence cube size is smaller than the RVE (or RAE) for composition. However, the size ratios of cubes and RVEs for composition (about four times maximum grain size) are quite similar all over the testing range, as shown in Table 1. When it is assumed that the RVE/RAE size for a given configuration-sensitive descriptor is a certain (descriptor-sensitive!) factor exceeding the one for composition homogeneity, an unbiased comparison study would still be possible. At least trends should be considered reliable, therefore, in this preliminary study.

Table 1: Ratios of linear dimensions of cubes and RVE/RAEs for composition homogeneity

<table>
<thead>
<tr>
<th>Cement</th>
<th>W/C</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>C206</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>C319</td>
<td>0.49</td>
<td>0.52</td>
<td>0.55</td>
<td>0.57</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>C497</td>
<td>0.54</td>
<td>0.57</td>
<td>0.60</td>
<td>0.63</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

5 Results

5.1 Global results on structure

Figure 2 shows a selection of the cements and their 28-day-old SPACE-generated structures of hydrated cements, and of UCN for various technological parameters.
This type of information offers a visual perception on the UCN structures as functions of these technological parameters. Next step is the geometrical statistical (i.e., stereological) description of aspects of these structures, so that a comparative study can be conducted.

The simplest one is the configuration-insensitive volume fraction descriptor, $V_V$. Data in Fig. 3(a), pertaining to the average value of volume density in the cube, demonstrate the fineness of the cement to have a limited effect on this parameter at equal w/c ratio, especially at low values. The many tiny UCN only marginally influence this parameter. However, this is different for the average number density in the cube, or the number of nuclei per unit of sample volume, $N_V$. The sensitivity level was set at 0.01 μm; smaller nuclei are not expected exerting significant effects on the self-healing capacity. Results are presented in Fig. 3(b).
The same sensitivity level was maintained for the highly configuration-sensitive nearest neighbor surface-to-surface spacing (NNSSS). A single example is presented in Fig. 4(a) for w/c=0.2. Larger cubes would have yielded smoother curves, however also in shifts in average values.

Smoothening can also be achieved by averaging over a series of identical tests, maintaining average values. This is common practice in systematic research. These shifts can be compared with so-called “size effects” in fracture mechanics. The RVE/RAE size can be derived from large test series on different sample sizes, from which probability density functions of the desired descriptor are obtained. As stipulated earlier, this was not pursued in this preliminary study.

The different measures for the curve’s characteristic averages are approximately increasing linearly with w/c ratio, as depicted by Fig. 4(b). Hence, cement more completely hydrates at higher w/c ratio and the resulting smaller numbers of nuclei left unhydrated are as a consequence more remote from each other.

Figure 4: (a) Probability density functions of NNSSS of UCN in three cement pastes (w/c=0.2) and (b) Mean values of NNSSS-curves of cement pastes with increasing w/c ratios

5.2 Local results on structure

So far, the ITZ properties are globally characterized. They can be compared with global bulk values. Gradients in local values perpendicular to the aggregate grain’s surface have been determined for UCN, gel and porosity. As stipulated earlier, sampled areas are of sub-RAE size. Nevertheless, volume fraction gradient inside the ITZ is obtained in an unbiased way (accepting somewhat more scatter due to sub-RAE nature of experiments). Fig. 5(a) only shows as an example $V_{V}$-gradients of UCN in C497.

Figure 5(a) and other gradient structures of UCN, gel and porosity clearly reveal the wall effects in $V_{V}$, defining the extent of the ITZ. Order of magnitude of the ITZ’s extent for volume fraction is 10 μm (slightly increasing with w/c ratio, as shown earlier in [4]). The fractional volume density of UCN declines from bulk toward the aggregate surface. This is more pronounced with the lower w/c ratio. Although not demonstrated because of space limitations, an opposite conclusion can be drawn with respect to porosity. Fig. 5(b) presents the same data, however comparing the different cement types for the sole case of w/c=0.2.

The slope in the gradient structures is the steepest for the fine-grained cement, although leading roughly to the similar level in bulk volume density as earlier shown in Fig. 3(a).
Hence, low w/c ratio and high cement fineness basically promote arriving at higher volume densities in the proximity of the aggregate grain surfaces.

![Figure 5: Gradients in $V_V$ of UCN (a) in C497 for five w/c ratios and (b) for three cement paste finenesses (w/c=0.2)](image)

With low w/c ratio, Figure 3 demonstrated the finer cement to yield far larger global numbers of UCN despite the similar volume fraction. For the same low w/c ratio, the gradient in local number density is depicted in Fig. 6(a). It reveals number density increasing from surface of aggregate to certain level. Finer cement has high number density of UCN throughout whole range conforming to Fig.3(b).

![Figure 6: Gradients in (a) $N_V$ and (b) $S_V$ of UCN (w/c=0.2) for three cement finenesses (w/c=0.2)](image)

Figure 6(b) indicates surface area density, $S_V$, to be influenced by the fineness of cement at the same w/c ratio. It reveals finer cement has high surface area density as well. This parameter could be expected to relate to probability of self-healing, which will be discussed later.

6 Discussion

Influences are investigated in this paper of w/c ratio and cement fineness on the structure of UCN that is underlying concrete’s self-healing capacity. Volume fractions of UCN are marginally depending on cement fineness. They decline at increasing w/c ratios as depicted by Fig. 3(a). Volume fraction of UCN is becoming insignificant for w/c $\geq 0.4$, in agreement with Power’s model [17].
Obviously, the associated high water contents allow for more complete hydration, and, as a consequence, smaller amounts of UCN will be left. Compared to fineness of cement, w/c ratio is the dominating factor for the self-healing capacity of concrete as additionally shown by Fig. 3(a). At higher w/c ratio, in bulk and in ITZ alike, averages of NNSSS of UCN increase; nuclei are more widely spread.

The cement fineness level exerts significant impact on the number and surface area densities of UCN ($N_V$, $S_V$) within a limited range of w/c ratio, i.e., 0.2 to 0.4, as illustrated in Figs. 3(b) and 6(b). In this range, the finest cement (C497) reveals much higher number and surface area densities, which can be attributed to the initially large value of $N_V$ in the fresh state of the cement. On the other hand, the finer cement leads to lower averages of NNSSS of UCN despite the degree of hydration (DOH) being only slightly different.

These results are quite similar to those obtained with periodic container boundaries, representing bulk conditions. Space limitations prevent going into details, however. But for local configuration-sensitive information of cement paste, influence of the aggregate is significant. A relative high volume fraction of UCN and apparent high surface area density were found in ITZs of finer cement model paste versus coarser one (see in the range of 0~5μm of Fig. 5(b)).

The ITZ is most liable to crack formation [1, 18]. The probability of micro-cracks in these zones to interfere with the UCN can be expected depending at least on the volume fraction of UCN. Furthermore, a tendency of cracks to follow the external surface of the UCN was found experimentally [19, 20]. Baldie explains this phenomenon by conceiving the UCNs as strong inclusions in the hardened cement paste. Therefore, surface density, $S_v$, of UCN can additionally be assumed related to concrete’s self-healing capacity. Finer cements were found producing relatively high surface area density in ITZs. As a result, higher probability of self-healing is expected for concretes made by fine cement type.

This mechanical part of the self-healing capacity that deals with the direct interference of cracks and UCN could be quantitatively evaluated, but will not be discussed here because of space limitations. Spacing, size and number of UCN are all expected to be vital factors for self-healing capacity of concrete under such conditions.

7 Conclusions

A mixture of composition and configuration-sensitive descriptors of material structure can provide reliable quantitative information on the evolution process of UCN during maturation of a rage of cement pastes. This can be achieved by concurrent algorithm-based computer simulated systems, like SPACE.

The water to cement ratio (w/c) is a key factor for self-healing capacity of hardened concrete. For w/c ≥ 0.4, the amount of UCN is very limited. Hence, discussion on self-healing capacity of concrete is only sensible for a limited, but for HPC relevant range of w/c ratios (w/c ≤ 0.4).

Concrete made with finer cement has high surface area density and similar volume fraction (even higher in ITZs) of UCN for given w/c ratio, so that relatively high probability of self-healing is expected for such types of concrete.
REFERENCES