NUMERICAL STUDY OF ELASTIC PROPERTIES OF ITZ IN HYDRATING CEMENT PASTE

V. Šmilauer and Z. Bittnar

CTU in Prague, Faculty of Civil Engineering, Department of Mechanics, Czech Republic

Abstract

The interfacial transition zone (ITZ) represents a serious problem when homogenizing elastic properties of cement mortar or concrete. Although many mechanisms contribute to its origin and evolution, only the wall effect will be studied. Commonly accepted thickness of ITZ, as it appears around the aggregates, is in the range from 0 to 50 µm. Cement hydration program CEMHYD3D extended with the percolation filtering will be used for the reconstruction of the ITZ and following hydration. Imposing periodic boundary conditions and using FEM leads to effective homogenized elastic properties of ITZ. Depending on the cement fineness, the reduction of Young’s modulus against bulk paste was found up to 40% while Poisson’s ratio remained almost the same for the ITZ thickness of 24 µm. Validation on mortar samples shows that the results are in accordance with experiment.

1. INTRODUCTION

Detailed analysis of cement composites in last decades has shown the difference between the structure of bulk cement paste and the paste around aggregates, fibers or other larger objects. The transition region is generally called interfacial transition zone (ITZ) and plays important role in the cement-based materials, such as mortar or concrete. Several studies emphasized the role of ITZ in the case of drying shrinkage [1], transport properties [2] and elastic properties [2,3]. Speaking in terms of composite mechanics, the ITZ creates the separate phase that is distinguishable from the bulk one. On the other hand, the properties of ITZ phase may be derived from the bulk paste [4].

Unhydrated cement particles are generally loosely packed around any aggregate, as testified experimentally [5] and numerically [2]. Till today, there is no commonly accepted view of ITZ formation. Scrivener and Pratt [5] aimed to explain the ITZ formation as localized bleeding occurring during slight movement of particles. Reasonable and the most often used explanation of ITZ is due to so called “wall effect”. Typical aggregate size in mortar or concrete is at least one order higher than some bigger cement grain. Therefore, the aggregate creates a barrier, where no overlap of cement grains takes place. This wall effect of inefficient packing is believed to be one of the leading mechanisms for the formation of ITZ.
After mixing cement with water, a thin film develops at the surface of the aggregates. Right on the aggregate surface, the calcium hydroxide, short fibers of C-S-H gel or ettringite are observed [6]. Going further into the direction from aggregate surface, region of CH crystals or ettringite are typically found [5]. In high performance concrete (HPC), the thickness of ITZ is strongly reduced due to fine fillers and superplasticizers. Diamond and Huang [7] concluded common properties from ITZ observation:

1. higher porosity and permeability around an aggregate,
2. lower amount of unhydrated cement grains,
3. higher amount of CH with orientation parallel to the aggregate surface,
4. higher amount of ettringite,
5. reduced strength and stiffness.

The thickness of ITZ corresponds roughly to the median diameter of cement grain [2]. Therefore, the ITZ thickness is independent on water-to-cement ratio (wcr). Higher porosity in the ITZ requires that the wcr in the bulk cement paste is lower but on average corresponding to the initial wcr. In this paper, modeling of ITZ is based solely on the wall effect. Such approach corresponds to the items 1), 2) and we expect that item 5) will logically follow as a consequence.

2. CEMENT HYDRATION MODEL

Any cement hydration model should reflect at least four effects: cement composition, particle size distribution (PSD), curing regime and temperature. For the purpose of mesh generation, discrete rather than continuum type of model is preferred. Cement hydration model CEMHYD3D [8], developed at NIST, is based on cellular automata approach. The idea is to split up a microstructure into voxels (volume elements), typically with an edge of 1 µm. A voxel should be considered as a collection of specific chemical phase from the neighborhood while maintaining a stoichiometry of chemical reactions.

![Figure 1: A flowchart of CEMHYD3D model and the calculation of mechanical response, adapted from [8]](image)

The size of voxel determines the model resolution that should be small enough to capture the important undergoing processes, e.g. dissolution, transport and diffusion. Several
problems occur when discretizing such continuous microstructure, similar to the cement paste. Since the resolution is limited, very fine cement particles and pores cannot be captured locally. A flowchart of the model with associated mechanical loading is shown in Figure 1.

The 3D microstructure, forming representative volume element (RVE), consists of chemical phases that are implemented as an ID assignment to each voxel. The rules how to handle individual voxels are called cellular automata and they define how voxels dissolve, move and what happens on their collision. Cellular automata are combined with probabilistic functions that were found effective in the description within considered model [9]. Hydration products are, with certain probabilities, formed on the grains exposed to water contact and they nucleate in the available pore space.

Initial and random 3D periodic microstructure is reconstructed with the help of autocorrelation functions and typically contains four cement clinker mineral phases and forms of calcium sulfate, all as the digital spherical particles. The size of microstructure may be arbitrary, limiting the maximal cement grain that may be placed in. Model cycles can be mapped on the time axis using a parabolic relationship [8].

Any model of a random system brings two sources of error: statistical fluctuation and finite size effect [9]. Statistical error emerges in any random system due to its representation, e.g. small dimensions of a cement paste. Finite size of representative cube captures only a limited piece of material that means that the sample is not statistically homogeneous. This problem may be eliminated, when representative cube is compared to the one that is considered big enough. For the wcr in the range from 0.25 to 0.5, the size of 100 x 100 x 100 µm is suggested by the NIST authors [9]. Our recent results from elastic homogenization show that the reasonable size of RVE is around 50 x 50 x 50 µm [3].

This model of cement hydration brings also digital resolution problems. The smallest information unit is the voxel size of 1 µm, therefore any smaller size is considered only if the concentration around the neighborhood reaches that volume. This is also the case of fine capillary pores. Simulation revealed that digital resolution plays a significant role in transport issues such as diffusivity or permeability [9] but is not critical for elastic homogenization [3]. The proper size for the voxel lies probably in the range from 0.125 to 1 µm/voxel due to physical limitations [9].

3. ELASTIC HOMOGENIZATION

Generally, two techniques are known for the determination of effective properties within composites. First, the analytical methods homogenize properties based on explicit or implicit analytical formulae. The composite morphology is usually reduced to assumptions, such as sphere assemblage. Unfortunately, the properties of ITZ strongly depend on paste morphology that need a special treatment by means of numerical homogenization methods. In such particular case, the microstructure from the hydration model must be discretized in finite elements with assigned elastic properties to each of them. As opposed to analytical methods, the size and boundary conditions of the representative volume element (RVE) determines the effective properties of ITZ. Perfect bonding among phases is assumed during all calculations, except a sharp corner problem as will be explained later.

Table 1 summarizes isotropic elastic properties as used during calculation with the mean values and standard deviations. The results are mostly obtained from nanoindentation tests on
pure synthetic or clean materials, gathered from worldwide journals and summarized in [3]. The standard deviation reflects varying porosity of a phase. Aggregate properties, which are of minor interest during the ITZ homogenization, were chosen to be much stiffer than the rest of phases and with a small contribution to the shear stiffness. The isotropic properties were selected for a simplicity since the orientation of phases remains unknown. Therefore, a random orientation of phases is assumed.

Table 1: Intrinsic isotropic elastic properties of major phases [3]

<table>
<thead>
<tr>
<th>Phase</th>
<th>E [GPa]</th>
<th>ν [-]</th>
<th>Phase</th>
<th>E [GPa]</th>
<th>ν [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>135±7</td>
<td>0.3</td>
<td>Porosity</td>
<td>0.001</td>
<td>0.499924</td>
</tr>
<tr>
<td>C₂S</td>
<td>130±20</td>
<td>0.3</td>
<td>CH</td>
<td>38±5</td>
<td>0.305</td>
</tr>
<tr>
<td>C₃A</td>
<td>145±10</td>
<td>0.3</td>
<td>C-S-HLD</td>
<td>21.7±2.2</td>
<td>0.24</td>
</tr>
<tr>
<td>C₄AF</td>
<td>125±25</td>
<td>0.3</td>
<td>C-S-HID</td>
<td>29.4±2.4</td>
<td>0.24</td>
</tr>
<tr>
<td>Gypsum</td>
<td>30</td>
<td>0.3</td>
<td>FH₃</td>
<td>22.4</td>
<td>0.25</td>
</tr>
<tr>
<td>Aggregate</td>
<td>1000</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1 Mesh generation and numerical results

The FEM will be employed for the homogenization process. The simplest case for the mesh generation is the hexahedral (brick) element where the voxel from the hydration model corresponds to one hexahedral element. Figure 2 shows such typical RVE slice. A preliminary simulation on similar RVEs yielded stiff behavior at the beginning of hydration, during homogenization of elastic properties [3]. The reason lies in the connectivity, or percolation, of solid phases. Spanning clusters in Figure 2 are identified as connected solid voxels face-to-face and they form percolated RVE. On the other hand, isolated clusters are not attached to any spanning cluster and they must be disregarded in mechanical calculations, since they do not contribute to the shear stiffness. In the mesh generation, the isolated clusters are substituted by a water-filled porosity.

Figure 2: Typical RVE slice illustrating the connectedness in hydrating cement paste

The node displacements in the FEM do not necessary correspond to the face-to-face connection. In certain situations, the same node displacement can not be shared by all solid neighboring voxels. This corresponds topologically to the sharp corners, where the stress
concentration takes place. In order to avoid the refinement of the mesh, split nodes have been introduced, creating several nodes with independent displacements at one location. This situation is typical for early hydration stages, up to degree of hydration of about 0.3. Above this point, the solids in the RVE are already well connected, reducing significantly the amount of isolated clusters and sharp corners, Figure 3.

Figure 3: Possible separation in the split node among adjacent voxels where the solid phases are disconnected

Periodic boundary conditions were found as the most appropriate for elastic homogenization. The reason is in small scatter of values when changing the size of RVE. The nodal force contribution $F^e$, generating load of such RVE is:

$$ F^e = \int_B B^T D^e T dV, $$

where $B$ is the strain interpolation matrix, $D^e$ is the material stiffness matrix of element and $T$ is the matrix containing prescribed eigenstrains. From all finite elements, the global stiffness matrix $K$ and load vector $F$ is assembled and the set of equation solved by conjugate gradient method, with unknown node displacements $r$:

$$ Kr = F. $$

The stresses $\sigma^e$ on each element are calculated from the difference between strains $\varepsilon^e$ and eigenstrains in the vector form of $T$:

$$ \sigma^e = D^e (\varepsilon^e - T') $$

and the strains and stresses are averaged:

$$ \langle \sigma \rangle = \frac{1}{V} \int_{RVE} \sigma^e dV, $$

$$ \langle \varepsilon \rangle = \frac{1}{V} \int_{RVE} \varepsilon^e dV. $$
The relation between average stress and strain generally fits anisotropic behavior at the macroscale. In such particular case, there would be 21 elastic constants. More detailed analysis revealed that the ITZ is anisotropic only to a small extent and transition from anisotropic to isotropic material may be based on the same stored elastic energy:

\[ W = \frac{1}{2} \langle \epsilon \rangle ^T \langle \sigma \rangle = \frac{1}{2} \langle \epsilon \rangle ^T D \langle \epsilon \rangle, \tag{5} \]

where \( D \) is the stiffness matrix that contains wanted Young’s modulus \( E \) and Poisson’s ratio \( \nu \). In the case of aggregate presence in the RVE, the homogenization procedure is modified such that eigenstrains \( T' \) are prescribed only to non-aggregate phases. Strain and stress averaging is performed over the volume without the aggregate voxels.

### 3.1 Hervé-Zaoui scheme

The validation of ITZ may be performed on the level of cement mortar. For such purpose, the analytical homogenization scheme of Hervé and Zaoui [10] is chosen. The mortar level has a typical dimension in the order of mm [3]. Homogenized cement paste, ITZ and sand aggregate (and possibly entrained air) are only distinguishable phases at this level. The morphology of this composite resembles matrix-inclusion morphology, where cement acts as a matrix while the aggregate covered by the ITZ looks like an inclusion. The \( n \)-layered, self-consistent, concentric sphere assemblage is an appropriate analytical model, Figure 4, originating in the work of Hervé and Zaoui [10]. The compatibility of displacements and stress continuity at boundaries formulate \( n-1 \) sets of equations which may be extended by a condition of applied stress at infinity. The system of equations is solved by a recursive method, finally arriving to a homogenized equivalent medium around the spheres.

![Figure 4: Geometrical representation of Hervé-Zaoui scheme](image)

The number \( j \) in Figure 4 represents the spherical fine aggregate, 2 stands for ITZ and 3 is the cement paste. No gradation of elastic properties in the ITZ is considered. The ratio of radii in the sphere assemblage should correspond to volume fractions of individual phases. Therefore, an average sand diameter, its volumetric content and ITZ thickness need to be specified before any calculation.
4. VALIDATION AND DISCUSSION

The analysis of ITZ is based on two RVEs, corresponding to loose and dense microstructures. The region of possible limiting combination is also reduced to two finenesses, yielding two RVEs of loose + coarse and dense + fine topology. German cements served as the reference cements from the NIST database, where PSD, autocorrelation functions and clinker minerals were measured [8]. Table 2 summarizes basic properties.

Table 2: Cement parameters for initial RVE generation

<table>
<thead>
<tr>
<th></th>
<th>Loose (and coarse)</th>
<th>Dense (and fine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wcr</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Blaine fineness</td>
<td>197 m²/kg</td>
<td>608 m²/kg</td>
</tr>
<tr>
<td>NIST reference cement No.</td>
<td>16155</td>
<td>16130</td>
</tr>
<tr>
<td>Median diameter</td>
<td>21 µm</td>
<td>3 µm</td>
</tr>
<tr>
<td>C₃S</td>
<td>0.7633 vol.</td>
<td>0.8100 vol.</td>
</tr>
<tr>
<td>C₂S</td>
<td>0.0892 vol.</td>
<td>0.0408 vol.</td>
</tr>
<tr>
<td>C₃A</td>
<td>0.0825 vol.</td>
<td>0.0875 vol.</td>
</tr>
<tr>
<td>C₄AF</td>
<td>0.0652 vol.</td>
<td>0.0617 vol.</td>
</tr>
<tr>
<td>Hemihydrate added as</td>
<td>5.4 % vol.</td>
<td>5.4 % vol.</td>
</tr>
</tbody>
</table>

The size of RVE was selected as 50 x 50 x 50 voxels that seems to be reasonable size for an analysis of elastic properties [3]. Moreover, the results were reconfirmed by generation of three different RVEs, simulating random nature of microstructure. Figure 5 shows a typical 2D RVE slice, showing the aggregate plane in the middle with the thickness of 2 µm.

The hydration program CEMHYD3D run with standard parameters and with the routine to separate two forms of C-S-H [3]. The sealed conditions and isothermal temperature of 20 °C were used as the model input.
4.1 Distribution of porosity and cement around aggregate
The RVE reflects the wall-effect topologically, i.e. decrease of volumetric fraction of porosity from aggregate and increase of cement content, Figure 6. The point where the ITZ characteristic changes to the bulk one coincides with the median diameter, Table 2. Therefore, the thickness of ITZ is dramatically different in both cases. However, the elastic homogenization inputs usually neglect this fact and assume constant thickness of ITZ regardless of median diameter.

Figure 6: Volumetric fractions from aggregate surface, loose and coarse (left) and dense and fine (right), note coincidence with median diameters of 21 and 3 µm

4.2 Elastic properties
The RVE size of 50 x 50 x 50 µm (or voxels) and the aggregate thickness of 2 µm result in the ITZ thickness of 24 µm. This value is close to the value of 25 µm which is considered as average between 0 and 50 µm. However, arbitrary ITZ thickness may be simulated. One has to bear in mind advantageous periodic boundary conditions that restrict us to maximal cement grain to be placed inside the RVE. On the other hand, non-periodic boundary conditions may solve this problem, resulting into much higher scatter of results.

Figure 6: Evolution of Young’s modulus in bulk cement paste and ITZ with thickness of 24 µm in loose and coarse (left) and dense and fine (right) RVEs as calculated via FEM homogenisation
Figure 6 shows the difference in Young’s moduli from FEM simulations. Each simulation has been performed three times, for different cement grain configuration in the initial microstructure, to simulate the random nature of cement paste. Each analyzed point contains standard deviation of three tests to illustrate small scatter of results. The relative reduction of Young’s modulus in the coarse paste is maximally by 17% and by 40% in the fine paste. The difference in early ages is small due to the fact that a lot of porosity exists everywhere in the RVE and increased amount in the vicinity of aggregate does not change results considerably. This is typical for the loose RVE even for higher hydration degrees but changes quickly in the dense RVE. It must be again emphasized that perfect bonding between aggregate and solid phases is assumed in the homogenization so additional reduction may arise from imperfect bonding or pore channels around an aggregate.

To demonstrate a weak anisotropy of results, fine cement at the degree of hydration of 0.9 was analyzed in more detail. Six loading cases yielded symmetric stiffness matrix with all elements, some of them being close to zero. Equation (5) is used to convert the results to the isotropic case.

Table 3: Example of anisotropic stiffness matrix for fine cement at the degree of hydration of 0.9

<table>
<thead>
<tr>
<th></th>
<th>49.4</th>
<th>14.64</th>
<th>14.02</th>
<th>~0</th>
<th>~0</th>
<th>~0</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.64</td>
<td>46.07</td>
<td>14.03</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>14.02</td>
<td>14.03</td>
<td>45.0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>14.93</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>15.75</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>16.12</td>
<td>~0</td>
</tr>
</tbody>
</table>

The Poisson’s ratio in bulk cement paste and ITZ is very similar, with slightly higher values in the case of ITZ, Figure 7. Although Young’s modulus and Poisson’s ratio are useful engineering constants, the bulk and shear modulus give more realistic information about behavior. Indeed, the bulk modulus has similar evolution as the Young’s modulus and shear modulus of ITZ is always lower.

Figure 7: Evolution of Poisson’s ratio in bulk cement paste and ITZ with thickness of 24 μm in loose and coarse (left) and dense and fine (right) RVE
4.3 Yang’s experiment on cement mortar

The effect of ITZ will be at validated on a typical, well hydrated cement mortar. The data from Yang [4] will be used in order to be able to reproduce his results via presented $n$-layered homogenization scheme. He assumed the average diameter of Ottawa sand as 450 µm, the thickness of ITZ being 20 or 40 µm. Ordinary Portland cement paste with water to binder ratio of 0.3 (including silica fume) has Young's modulus of 20.76 GPa, Poisson's ratio of 0.2. Young's modulus of aggregate was determined as 80 GPa, Poisson's ratio as 0.21. He measured experimentally elastic response of that mortar, containing volume fractions of sand aggregates as 0, 0.1, 0.2, 0.3, 0.4, and 0.5.

![Graph](image)

**Figure 8:** Results from homogenization on the mortar level with 20 (left) and 40 µm (right) ITZ thickness and various Young’s moduli reduction in ITZ.

Yang [4] found, using different homogenization scheme that increasing the ITZ thickness is somehow equivalent to increasing elastic modulus of ITZ zone. For the ITZ thickness of 20 µm he found Young’s modulus between 0.2 - 0.4 of cement paste and for the thickness of 40 µm, he deduced that Young's modulus lies between 0.5 and 0.7 of that of bulk paste, respectively. Poisson’s number is considered to remain the same during the reduction procedure, which agrees well with our homogenization results. Figure 8 shows the results with reduced Young’s moduli in the ITZ for 3-layered concentric spheres. The reasonable reduction of Young’s modulus in the ITZ seems to lie between 0.5 and 0.6 for 20 and 40 µm thick ITZ. These results are in accordance with Neubauer et al. [1].

5. CONCLUSION

Cement hydration program combined with elastic homogenization has been presented and applied for the determination of ITZ properties, accounted only for the wall effect. Reduction of Young’s modulus was observed in coarse and fine cements, up to the value of 40 % against the same bulk cement paste when 24 µm ITZ thickness was assumed. Poisson’s ratio remained nearly the same in both bulk paste and corresponding ITZ. Validation on mortar samples showed perfect agreement with results when the Young’s modulus was reduced to
50 % with ITZ thickness of 20 µm. The wall effect remains probably the leading mechanism in terms of elastic properties. Other factors may contribute to further reduction of Young’s modulus, e.g., imperfect bonding with aggregate or different morphology in the ITZ.

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