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Multi-scale hydration modeling of calcium sulphates

Computer models for cement hydration has been proven to be a useful tool for understanding the chemistry of cement hydration, simulating the microstructure development of hydrating paste and predicting the properties of the hydration process /1/. One of these advanced models is CEMHYD3D, which is used and extended within the University of Twente for the last 12 years with pore water chemistry /2/, slag cement /3/ and multi-time modeling /4/. Chen and Brouwers /5/ pointed out that the smallest size handled in CEMHYD3D, called the 'system resolution' is important for a digitized model. Features smaller than the voxel sizes cannot be represented since the model works based on the movement and phase change of each discrete voxel. Furthermore, the system resolution determines the amount of computing time needed for a specific task, a higher system resolution will lead to longer computational time. Due to better computational possibilities, the use of higher resolutions is possible nowadays.
This article shows the effects of using different resolutions with CEMHYD3D. This is done for the 'fresh' mixtures as well as during hydration modeling of the binder. The model has been modified to cope with several different resolutions from 0.20-2 µm (or 500-50 voxels in the system in a box of 100 µm x 100 µm x 100 µm). This paper shows two methods for the multi-scale modeling. The first method consists of a system, which use a modified PSD-line for each resolution. The second method uses the same digitized initial microstructure, but in stead of 1 voxel of 1 x 1 x 1 μm^3 for 200 µm-system 8 voxels of 0.5 x 0.5 x 0.5 μm^3 are used and for the 300-µm system 27 voxels of 0.33 x 0.33 x 0.33 μm^3.

First method

The modification contains several steps starting with the digitalization of the particle size distribution, the preparation of the initial microstructure and modification of the model.

Particle size distribution

The first step is to digitize a real particle size distribution (PSD), so it can be used in CEMHYD3D. Therefore the continuous particle size distribution is divided into small sieves/steps. The number of sieves depends on the chosen system resolution. The higher the resolution the more different particles are available and therefore the more sieves will be used for digitizing the PSD. When the difference of the sieve sizes is small, the digitized PSD is again almost continuous. The last sieve contains all particles bigger than the upper limit. During the current research an upper sieve of 40 µm is used. Figure 1 shows the PSD at different resolution compared to the real PSD. It can be noticed that the digitized PSD shows a very small deviation from the real PSD. The differences are the result of the stepsize of the sieves and smallest sieve size. The lower limit is equal to size of the smallest discrete particle and so is the used resolution. A lower resolution creates the possibility to model the smaller particles. In the case of 0.2µm resolution the smallest particles can even be found of the first sieve and no particles can be found in the bottom sieve.

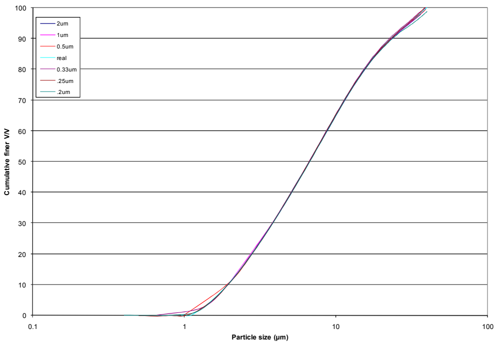

Fig. 1: Digitized and real PSD

Specific surface of the particle size distribution

Besides the fineness of the powder, also the surface area of the particles plays a role in the hydration process. In this section the specific surface area (SSA) of the powder based on the PSD is determined. The shape of the particles has an influence on the SSA. The shape of particles is described by the shape factor F /6/. In ideal situation the particles are spherically shaped (F = 6). The simulated hemi-hydrate particles used have a sphericity of 1.18-1.3 /6/. This corresponds to a shape factor of 7.08-7.8.

The particles within CEMHYD3D are digitized. An example of particle used in CEMHYD3D is shown in Figure 3. Their shape factor depends on the particle size, but is approximately 9 for the larger particles. Figure 2 shows the results the SSA of the created digitized PSD's for both spheres and digitized particles. It can be noticed from Figure 2 that the SSA based on the spherical assumption (with F = 6) is lower than the digitized particles. When assuming the shape factor given by Hunger and Brouwers /6/ for gypsum a higher SSA is found.

Preparation of the initial microstructure

This section will focus on the effect of the water/gypsum-ratio (wgr) and the system resolution on the specific surface area. Therefore the created particle size files are converted in number of particles and these particles are equally dispersed through the

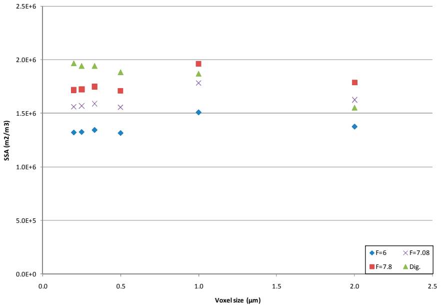

Fig. 2: Real particle size vs SSA

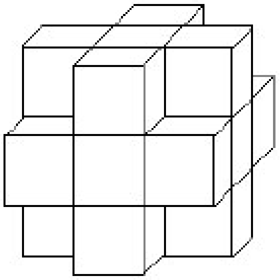

Fig. 3: Diginitized particle /2/

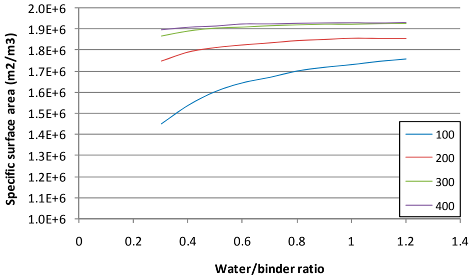

Fig. 4: Wgr versus SSA

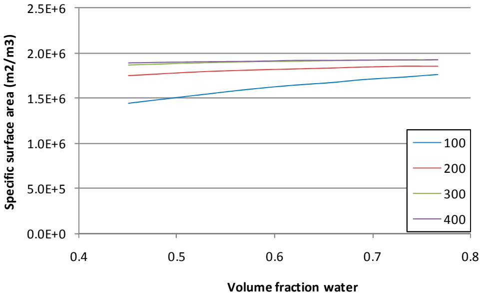

Fig. 5: Volume fraction water fresh mixture versus SSA

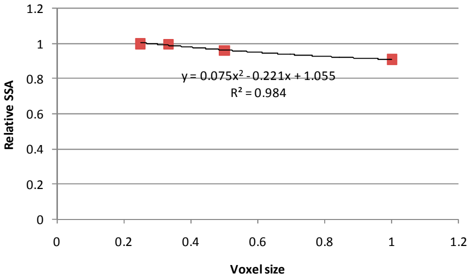

Fig. 6: Voxel size versus relative SSA

matrix using the makecem-module of CEMHYD3D. The SSA of the created microstructure have derived by counting of the surface, which is in direct contact with the voids. Figure 4 shows the results of this analysis. It can be noticed from Figure 4 that the wgr influences the SSA strongly. At lower wgr's, there is a higher amount of interconnection between particles and therefore a lower SSA. For wgr = 1.2, the SSA is comparable to the PSD-based version from the previous section.

It can also be noticed that the SSA of the 0.33 µm and 0.25 µm system are almost the same. This indicates that a smaller resolution than 0.25 µm will not lead to better results. Unfortunately due to shortage in memory, the results for the 0.2 µm system could not be obtained. But based on Figure 2, it can be assumed that the results of this simulation would be comparable to the 0.25 and 0.33 µm system.

Figure 5 shows the results when comparing volume fraction water to SSA. The volume fraction water has been derived based on the equations of Schiller /7/ and Brouwers /8/. It was shown by Yu et al. /9/ experimentally that these equations are valid for gypsum-based materials, both in fresh and hardened state.

Figure 6 shows the relation between voxel size and the relative SSA. The relative SSA is the digitized SSA divided by the real specific surface area. It can be noticed that when the voxel size becomes smaller, the relative SSA goes to unity. This can be expected since the PSD becomes more continuous when the sieve-steps become smaller.

Hydration results

The hydration model has also been modified for smaller voxel sizes. The dissolution and nucleation chances, the maximal number of diffusing particles all have been modified. This section describes the effect of the change of the resolution on hydration rate, temperature, dissolution rate and specific surface change during hydration.

Figure 7 shows the hydration rate of the system at different resolutions. It can be noticed that the hydration rate is lower for the higher resolutions. This is probably caused by a slower dissolution of the hemi-hydrate particles. This is confirmed by Figure 8, which indeed shows a lower decrease of the volume fraction hemi-hydrate for the higher resolutions.

The starting surface area of the higher resolutions based on the previous section is slightly higher for the higher resolutions, so the SSA cannot be the explanation for the slower dissolution of the hemi-hydrate particles. All studied parameters show that the hydration rate is lower to due to lower dissolution of the gypsum at higher resolution. Since gypsum hydration is a through-solution process, this is the limiting factor. The modeling of the dissolution chance of hemi-hydrate has been checked extensively, but up to now the reason for the difference between the different system resolutions is not yet found.

There is a possibility to acquire comparable hydration rates at different system resolutions. In order to get these comparable hydration rates, the time-axis of 200 µm-system have to be multiplied by 0.5 and time-axis of 300 µm-system have to be multiplied with by 0.33. Figure 9 shows the results of this modification. So when the cycles to time is corrected for the modified system resolutions, agreement is obtained

Second method

This method split the smaller voxels of the initial microstructure into smaller voxels. Figure 10 shows the same particle as Figure 3, but at a higher resolution.

Figure 11 shows the hydration rate of systems according to second method. It can be noticed that the higher resolution results in a lower hydration time. When the hydration time of 200 µm system is multiplied with 0.5 and 300 µm-system with 0.33, the hydration curves are again comparable. This is shown in Figure 12. The reason for the need of this correction factor is not yet found, but it turns out that with this correction of the cycles to time, agreement is obtained for the different resolutions.

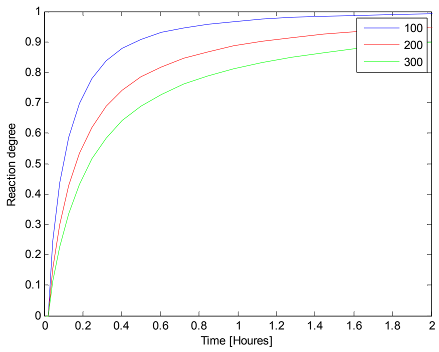

Fig. 7: Hydration rate (wgr = 0.80)

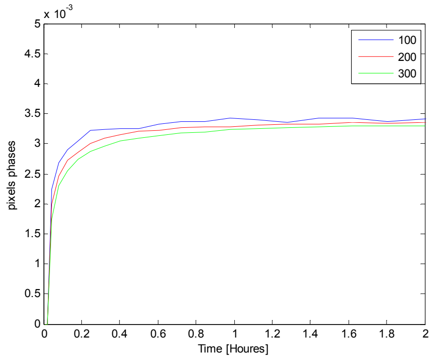

Fig. 8: Normalized now diffusing gypsum

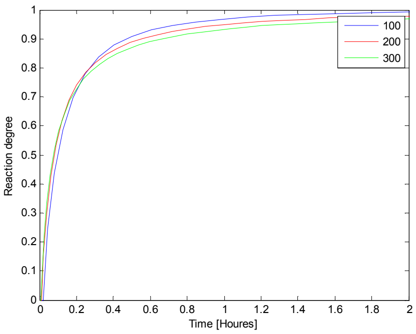

Fig. 9: Corrected hydration rate

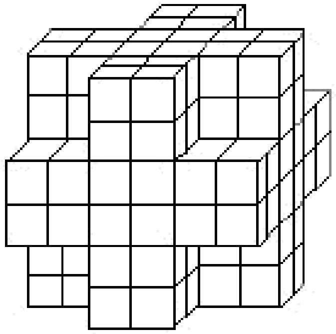

Fig. 10: Higher resolution particle

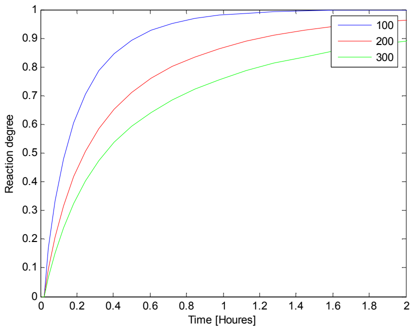

Fig. 11: Hydration rate (wgr = 0.80)

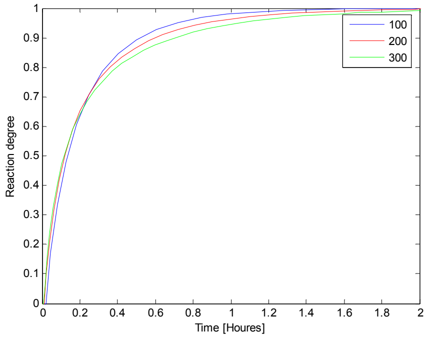

Fig. 12: Corrected hydration rate (wgr = 0.80)

Conclusions

This article reveals that the possibility to use different system resolutions in the CEMHYD3D, applied to the hydration of gypsum. The main findings were;

- The created digitized particle size distributions at different system resolutions shown comparable results.
- The specific surface area based on the PSD show that the SSA improves when a lower system resolution is used.
- The SSA of the initial microstructure (‘fresh mixtures’) show that the SSA is less influenced by the wgr for the higher system resolutions.
- The hydration rate for the higher resolutions is lower, although the specific surface is higher.
- The used simulation model on the moment provides different hydration rates, when the resolution differs. When the hydration rates are multiplied by 100 divided by the system resolution, the hydration curves are comparable when the use of both the first and second method.
- The second methods seems to provide the best results up to now, this is probably the result of the elimination of several differences between the initial microstructures (i.e void fraction, specific surface area).

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