Shape analysis of a reference cement

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Communication

Shape analysis of a reference cement

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Abstract

Recently, techniques for acquiring, analyzing, and using 3-D shape information for aggregates (sand, gravel) have been developed and demonstrated. These mathematical techniques, based on spherical harmonic coefficient analysis, have been applied to X-ray computed tomography images. X-ray microtomographic images of cement particles are required to be able to apply these same mathematical techniques to analyze Portland cement particle shape. Such images are available in the Visible Cement Database for a single reference cement. Actual cement images, as well as some quantitative results on the nonsphericity of the particles, are given here. Three-dimensional cement particle shapes have never been available before. A demonstration of how real cement particle shapes will change the CEMHYD3D cement hydration model is also given.
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1. Introduction

Once an adequate resolution 3-D image of a particle has been obtained, a recent paper has demonstrated how to use mathematical techniques to analyze the image using the coefficients of the spherical harmonic series [1]. Using these coefficients, an accurate image of the particle can be visualized, rotated, translated, and shrunk/expanded [2]. Adequate resolution means that there should be at least about 5 to 10 voxels per unit length in all three particle dimensions. A voxel is a small cube that forms the basic element of a 3-D digital image, in the same way that a square pixel is the basic element of a 2-D digital image.

If the approximate particle size in any one dimension is x, then, the voxel size should be about $0.1x$. A midrange fine aggregate is about 1 mm in size, so that an adequate resolution for it would be 100 μm/voxel, which is an easily obtainable figure for most X-ray-computed tomography scanners. However, for Portland cement, with a mean size of about 15 μm, an adequate resolution is then in the range of 1.5 μm/voxel. This resolution can only be obtained by the best X-ray microtomography synchrotron sources.

Recently, a paper and companion web site has appeared, entitled *Visible Cement Database* [3], which presents the results of an X-ray microtomographic study of cement paste. The X-ray microtomography beam line at the ESRF facility in Grenoble, France was used to gather 3-D images, at a resolution of 0.95 μm/voxel (cubic voxels), of a standard reference cement, CCRL-133, from the Cement and Concrete Reference Laboratory [4]. The cement had a Blaine fineness of about 350 m^2/kg. Images were taken of the cement paste microstructure at various ages to compare with the output of the CEMHYD3D cement hydration model [5], which is usually run at nearly the same resolution, 1 μm/voxel. Image acquisition of the unhydrated cement particles was attempted, but because of the motions of the cement particles in the water, only clear images were obtained after 3 h of hydration. At this point, only a few percent by volume of the cement had hydrated, just enough to cause set [6]. These images could be analyzed, and the hydration products identified and removed. What was left after this process were the cement particles (except possibly the very finest particles having diameters on the order of a micrometer or less), which are very close to their original shape. It is this image that has been analyzed to numerically acquire cement particle shapes, quantitatively analyze the shapes, and visualize the shapes in 3-D. Thus, for the first time, individual cement particle shapes can be seen in 3-D. Some surface modification might have taken place due to surface

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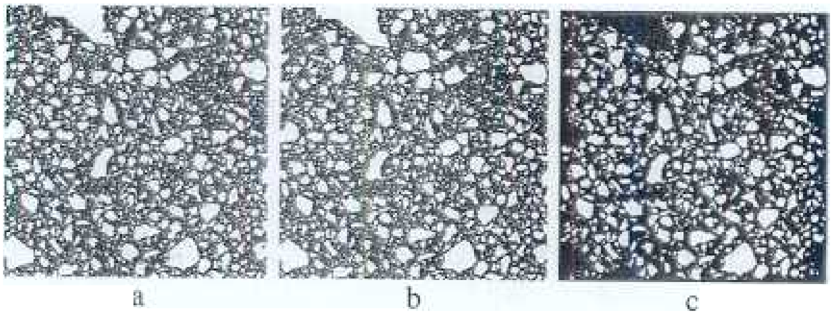

Fig. 1. (a) A slice cut out from the original binarized tomographic image, (b) the same slice after internal porosity has been removed in 3-D, and (c) the same slice after artificially cut particles and small particles with volumes below 125 voxels (in 3-D) have been removed.

hydration, even for the larger particles, but the scale of the image, 0.95 μm/voxel, probably would not have picked up this small change.

2. Data and techniques

The Visible Cement Database web site, where all the data gathered may be obtained (http://www.visiblecement.nist.gov), contains the 3-D images constructed out of the many slices generated in X-ray microtomography. The full 3-D images are 1024^3 voxels in size. Various programs for manipulating the images, which were used to identify and eliminate the hydration products, can be obtained from the site.

The images are in the form of circular cylinders embedded in rectangular cylinders. The data used were the *pt045-h-3hv1c300* and *pt045-h-3hv2c300* files, which were the top and bottom halves, respectively, of a CCRL-133 sample with w/c = 0.45 paste and hydrated for 3 h. These images were combined, and then, a $600 \times 600 \times 800$ voxel piece was cut out and saved. This was the largest piece of the image that stayed away from the sample cylindrical boundary. A sweep of various programs [1,2] was made through this image, eliminating particles that had been cut (hence, did not have a realistic shape) and that were too small (less than 125 voxels in volume). Internal porosity, which was mainly an artifact of the X-ray microtomography process, was also eliminated. Fig. 1 shows an original slice (Panel a), the same slice after internal porosity has been removed (Panel b), and the slice after artificially cut and small particles have been removed (Panel c).

Spherical harmonic analysis was applied to each particle, and further error checking was used to eliminate multi-particles, which are two or more particles that have been artificially welded together by the X-ray microtomographic reconstruction process [7]. There were over 60,000 particles with voxel volumes greater than 125 in the original processed image. Only particles with voxel volumes greater than 2000 were further processed, so as to leave a margin of error above the 10 voxels/unit length cutoff and, also, to reduce the number of particles considered. About 1200 particles were processed, and their spherical harmonic coefficients stored. A voxel volume of 2000 corresponds to a real volume of 1715 $\mu m^3 = 2000(0.95\ \mu m)^3$. If that number is set equal to the volume of a sphere, then, the diameter of the sphere that has equal volume is called the equivalent spherical diameter, which is 15 μm in this case. The maximum particle size was an equivalent spherical diameter of about 60 μm.

3. Qualitative and quantitative results

Fig. 2 shows two views each of different cement particles. The images were taken from a VRML browser. The VRML files are automatically generated from the spherical harmonic expansion [2].

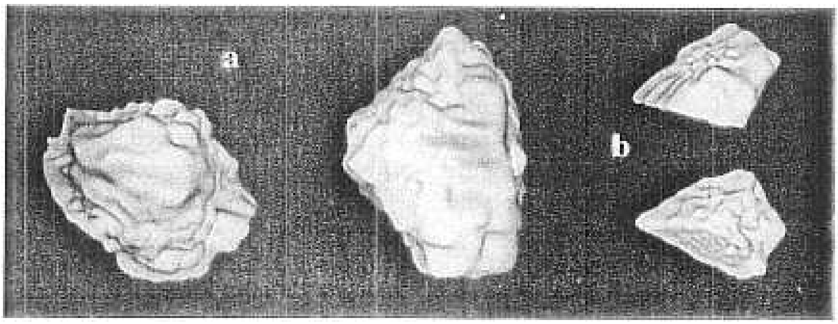

Fig. 2. Two views each of two CCRL-133 cement particles: (a) equivalent spherical diameter of about 36 μm, (b) equivalent spherical diameter of the particle of about 15 μm.

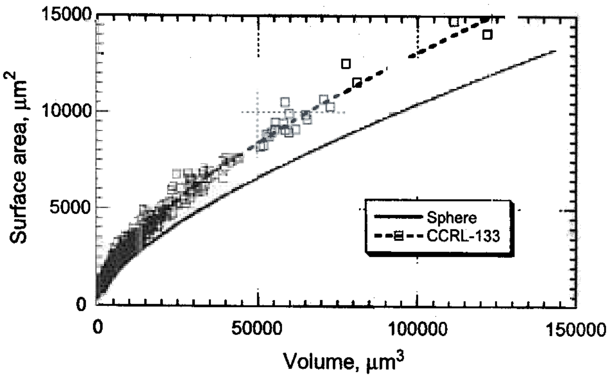

Fig. 3. True surface area versus true volume for all 1200 CCRL-133 cement particles analyzed. The solid line is the theoretical relation for a sphere, $S=(36\pi)^{1/3}V^{2/3} \approx 4.84V^{2/3}$. The dashed line is a power law fit of the form $S=8.0V^{0.64}$.

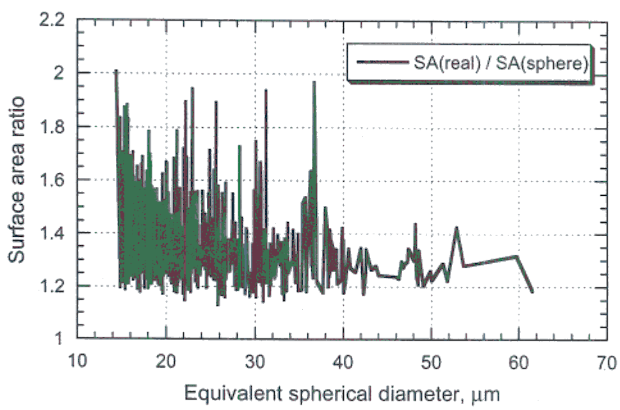

Fig. 4. A graph of the true surface area of each particle divided by the surface area obtained from the sphere with the equivalent spherical diameter, versus the equivalent spherical diameter.

One way to quantitatively analyze the shape of a collection of particles of various sizes is to plot their surface area versus their volume. For a sphere, the surface area S, in terms of the volume V, is $\approx 4.84V^{2/3}$. Deviations from this curve are a measure of the nonspherical nature of the particles. It is known that a sphere has the minimum surface area for a given volume for convex shapes in 3-D [8], hence, the curve for these cement particles should lie on or above the sphere curve. Fig. 3 shows these data along with the theoretical curve for a sphere. A function has been fit to the cement particle data of the same form as the theoretical function for a sphere: $S=aV^b$. The value of b was found to be 0.64, and the value of a was 8.0. There was about 10% uncertainty for both of these numbers, and the R^2 value of the fit was .98. The particles are definitely nonspherical, although the variation of surface area S with volume V is qualitatively similar with that of a sphere, in terms of the power law, but with a different prefactor. This would imply that the fracture surfaces of these ball-mill crushed particles, at this length scale, are not fractal but are close to Euclidean, because the error bars for the fitted exponents include the Euclidean exponent of 2/3. Therefore, the shape differences seem to show up in the prefactor, not in the exponent. Since the reaction of cement particles with water takes place initially at the particle surface, it would seem important to model the shape of the cement particles accurately in any cement hydration program.

Since cement particles are obtained by grinding much larger cement clinker particles, one might think that the smaller particles, which may have been ground more, would tend to be more spherical in shape. This would tend to be true for homogeneous material. On the other hand, small particles may be fragments knocked off a larger particle that were never ground much more due to their small size. In addition, Portland cement is not homogeneous.

Fig. 3 showed an overall shape analysis for all the particles. One way to estimate the nonsphericity of an individual particle is to compute the ratio of the true surface area to the surface area of a sphere having the equivalent spherical diameter. If V is the true volume of a particle, then, the equivalent spherical diameter is $(6V/\pi)^{1/3}$, and thus, the surface area of a sphere with this diameter is $S=\pi^{1/3}(6V)^{2/3}$. This surface area ratio is, of course, unity for a sphere. As this surface area ratio increases from one, the particle is increasingly nonspherical. Fig. 4 shows this ratio, plotted

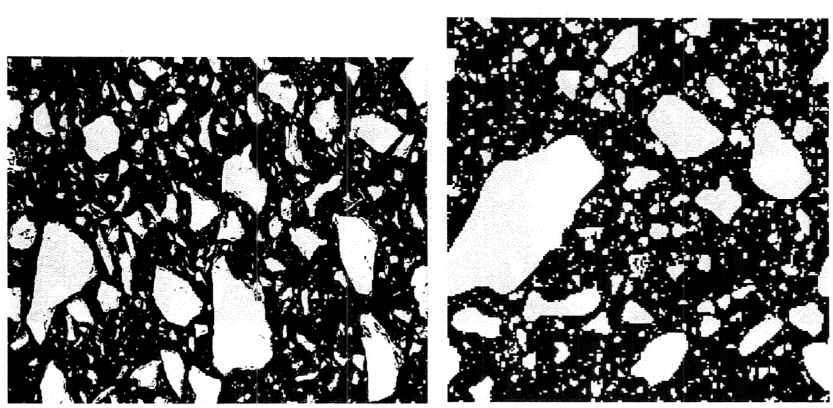

Fig. 5. The left panel shows an SEM image of real cement particles, while the right panel shows a slice from a simulated 3-D cement particle packing, using real particle shapes.

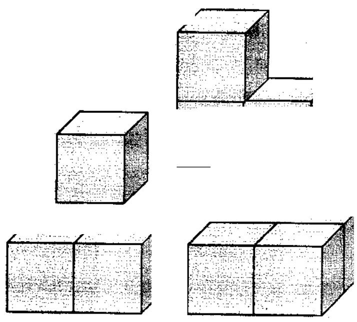

Fig. 6. Particle shapes used for volumes less than 5 voxels.

against the equivalent spherical diameter, which is used as an approximate and convenient measure of particle size. While there is a lot of noise in these data, one can see that the smaller particles seem to have ratios bigger than those of the larger particles and, hence, are less spherical than the large particles. This can probably be attributed, as was said above, to the inhomogeneous nature of Portland cement, with different values of hardness for different phases.

In the CEMHYD3D model, spherical particles are randomly placed into a unit cell. The diameters of the particles follow an experimentally measured particle size distribution, and the chemical phases in each particle are statistically assigned according to experimentally measured correlation functions in 2-D. Now that we have the real particle shapes, at least for the medium and larger particles, it is interesting to place real-shaped particles in a model microstructure, and then statistically place within them the chemical phases, as measured on real particles by scanning electron microscopy and X-ray point analysis [5,9].

Fig. 5 shows a polished section of a real cement/epoxy image (left) and the right panel shows a slice of a model 200^3 voxel microstructure, 0.5 μm/voxel, where real cement particle shapes, as denoted by spherical harmonic coefficients, have been used for model particles. The model microstructure was made by randomly choosing from the 1200 cement particle images and shrinking or expanding each in size to match a typical experimental cement particle size distribution. Particles were digitized before placement in the matrix. Particles whose voxel volume, after digitization, was 5 or more voxels, remained as they were. Particles with less than 5 voxels in volume were assigned randomly oriented shapes, as shown in Fig. 6, because in the digitization process, the original shape information is lost for these small shapes. For the 3- and 4-voxel particles, other shapes are possible and will be investigated for incorporation into the next version of CEMHYD3D. Obviously, for particles this small, there are digital lattice effects.

Finally, we can assign chemical phases, just like what has been done with spherical particles. The programs that assign phases operate on digital images of particles and, hence, do not "know" whether the particles are spherical or nonspherical because the particles are just collections of voxels. Fig. 7 shows a single slice from the result of performing this operation for CCRL-133 in 3-D. In the figure, white = C_3S, black = porosity, and the descending gray level (from white to black) = C_4AF, C_2S, and C_3A (C = CaO, H = H_2O, F = Fe_2O_3, A = Al_2O_3, and S = SiO_2).

4. Conclusions and future work

A number of years ago, the progress of CEMHYD3D was such that bulk cement chemistry was insufficient to track the course of hydration accurately. The phase composition within thousands of particles was then measured by a combination of scanning electron microscopy and X-ray microprobe mapping and was statistically built into model 3-D particles [5]. These model particles were still only spherical, however, although 2-D cross-sections of cement

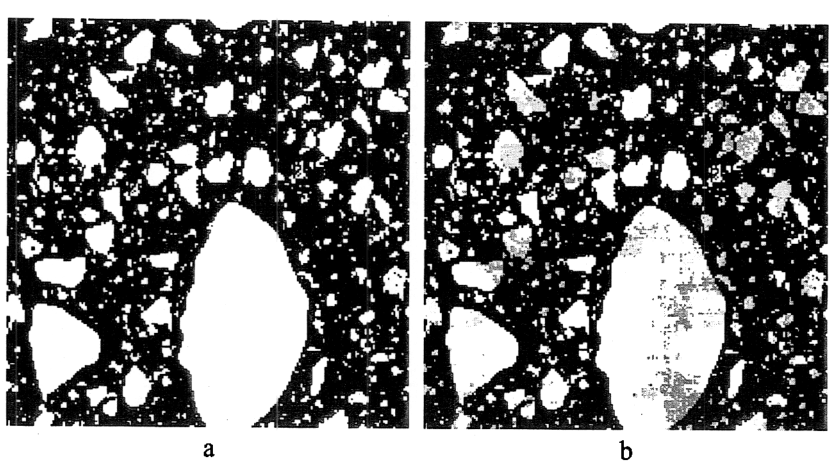

Fig. 7. (a) Cement microstructure, without chemical information (different slice from Fig. 5 and (b) the same image but with the four standard Portland cement clinker phases distributed throughout the basic cement particles by using the Virtual Cement and Concrete Testing Laboratory. Note that in several places in the image, two particles appear to be stuck together, which is often seen in real images and which can be seen in the left panel of Fig. 5. White = C_3S, black = porosity, and descending gray level (from white to black) = C_4AF, C_2S, and C_3A.

particles, seen in scanning electron microscopy, were clearly not circular. Now, this shortcoming can be overcome. The actual 3-D shapes of cement particles have now become available, at least for one kind of cement. Future work is planned at X-ray microtomography sites to collect more cement image data at 1 μm/voxel or smaller resolutions.

It is interesting to see these shapes dredged up from the deep, so to speak, but it is even more interesting to see what effect shape has on cement and cement paste and, eventually, concrete properties. There is some evidence that different cements have different water demands—this may be due to shape and, thus, surface area differences. Any physical property differences between the same cement ground in a ball mill versus a roller mill should be due to the almost certain particle shape differences between cement powders made with these two processes. Of course, there may also be changes in the gypsum form due to temperature differences between the grinding techniques. The effect of different grinding aids and grinding time on particle shapes and how the shapes are distributed with respect to size are interesting questions, which, at the 5- to 10-μm particle size level or above, can now be explored. The increased use of cement particle shape data, as well as quantitative particle size distribution measurements [10], should greatly accelerate the development of the computational and experimental materials science of cement and concrete.

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