Computer simulation of interfacial packing in concrete

M. W. GRUTZECK, D. SHI, G. LIU*, S. KWAN
The Pennsylvania State University, Materials Research Laboratory, University Park, PA 16802, USA

Computer simulation of particle packing against an aggregate surface was undertaken to show the effects of four variables on interfacial porosity profiles. The variables in order of significance and their assumed physical meaning are: sticking probability (tendency of cement particles to flocculate), amplitude of particle motion (energy of mixing), travel distance of particle to surface (thickness of water film surrounding aggregate), and original particle density (roughly related to water/cement ratio). In all cases, simulations demonstrated that interface porosity decreased from nearly 100% directly at the interface to that of the bulk paste at two to three particle diameters. Flocculation (sticking probability) was found to be the single most-significant variable. Highly flocculated systems produced very porous interfaces. When flocculation was reduced, packing became more efficient. It was also found that energy of mixing (amplitude of motion), was not an entirely independent variable. The simulation showed that, if the tendency to flocculate was high, gentle mixing (low amplitude of motion) was found to result in better packing and a less porous interfacial zone. If, on the other hand, flocculation was low, then vigorous mixing (high amplitude of motion) promoted better packing near the interface. The thickness of the water film surrounding the aggregate (travel distance) was found to have only a minor effect on the outcome of simulations, while original packing density (w/c) resulted in no significant differences at all.

1. Introduction

The origins of the interfacial zone which develops between cement paste and aggregate in concrete can be visualized as a two-step process. During the mixing of concrete, micrometre-sized cement particles are brought into contact with the surfaces of both fine and coarse aggregate. Transport can occur either through air or a thin film of water. Once initial packing has taken place, subsequent chemical reactions occur between the cement particles and the surrounding water which ultimately fill the interparticle voids with hydration products.

To date, most of the experimental work reported in the literature has been descriptive, concentrating on exploring changes in bulk chemistry and porosity across the interfacial zone. Although this work is important, we feel that the observations are merely a reflection of the efficiency of the initial packing of cement particles against aggregate surfaces. Thus a knowledge of how particles pack against surfaces could be quite valuable to the cement chemist both in terms of explaining already documented material as well as a design aid to produce a better concrete.

Traditionally, an experimental approach has been used to examine the geometrical aspects of random packing [1–6]. For example, using mathematical modelling and experiments, it has recently been shown that denser packing of cements, sand and aggregate led to improved workability, and a stronger, less-permeable concrete [7, 8]. As powerful as the method is, comprehensive investigations were often not practical because the experiments were tedious and time-consuming. However, in the last two decades, computer simulation has become more and more of an attractive alternative [9–21]. The entire range of packing problems, including the packing of particles against surfaces, has been studied using such simulations.

It has been a long-held belief that, in composite materials such as concrete, porosity near the interface between different phases, e.g. cement paste and aggregate, is higher than that in the bulk material. Therefore, the higher porosity in the interfacial region is often viewed as detrimental. The high porosity near an interface between cement paste and aggregate has been quantified by using advanced image analysis techniques [22]. However, using experimental means alone, one is not able to identify the cause of the higher porosity near the interface. It can only be postulated that the local packing of cement particles near the surface of the aggregate is poor [23].

As we report below, by using computer simulations one can conduct numerous experiments in a relatively short time and in this way easily display the build-up

---

* *Present address:* International Software Systems, Inc. 9430 Research Boulevard, Echelon IV, Suite 250, Austin, TX 78758, USA.

of high porosities near a surface, porosities which can be attributed to the so-called wall effect [11]. Garboczi and Bentz recently used this approach to investigate the cement paste–aggregate interfacial zone in concrete [24].

The problem associated with using a computer simulation is how accurately it simulates a real process. All of the existing simulation methods invariably involve sequential addition of particles to an existing accumulation of particles. Normally, there is no interaction between particles. Programs of this type neglect phenomena such as flocculation, agglomeration, and clustering. For example, cement paste is always flocculated unless it is batched with an effective dispersant [23], and even in this instance, flocculation is not entirely eliminated. Our simulation is slightly different in that it was designed to emulate simultaneous packing of a large number of particles. Therefore, particle interactions could be built into the program. The degree of agglomeration is controlled by a user-definable parameter, referred to as sticking probability. It is worth noting that our computer program is more appropriate to model physical mechanisms (packing of hard spheres) rather than chemical mechanisms dealing with hydration and the development of pore structures. At early stages, after water and solid are mixed, other than surface protonation ($Ca^{2+} = 2H^+$), no significant chemical reaction occurs [25, 26]. Therefore, the initial packing of cement particles against the surface of aggregates can be considered to be mainly a physical process resulting from the mixing of dry ingredients with water.

For the purpose of this report, we are assuming that the aggregate is moist and that cement particle transport occurs through a thin film of water adhering to the aggregate surface. Depending on surface charges, the cement particles will experience different degrees of flocculation as they move towards the aggregate surface.

The following sections contain a description of the simulation algorithm and a series of simulated interfacial pore structures illustrating the effect of four variables (initial particle density, sticking probability, amplitude of motion and distance to aggregate surface) on interfacial porosity. Discussion will focus on the physical interpretations of the generated interface porosity profiles and other phenomena observed in the simulations. For example, one set of simulations suggests that a concrete which exhibits a large degree of flocculation would benefit from very gentle rather than vigorous mixing. In this instance, gentle mixing led to better packing and lower porosity at the interface.

2. Simulation algorithm

The program is written in C language and will run on an IBM or compatible with an EGA graphics adaptor. The build-up of particles at the interface can be followed by watching the monitor screen (see Fig. 1). The bottom line in this figure represents the aggregate surface, and cement particles are represented by spheres of equal or unequal sizes. The diameter and, if any, the distribution of sphere size, are user-definable. In this instance, they are all 12 pixels in diameter. (A pixel is the smallest spot a computer is able to define. Our monitor screen is 640 pixels wide and 350 pixels high.) Particles generated by the computer are placed at random in a rectangular area at a user-definable distance above the bottom line (aggregate). The size of the rectangular area and the original packing density are also user-definable. In this instance, the size of the rectangular area has been fixed at 640×150 pixels and packing density was varied from 0.4–0.2. Particles can be generated set by set or all at once. The next set of particles will be generated when the previous set of particles have settled at the interface. The total number of sets of particles is user-definable. In this instance we have used a single set of particles. The initial packing density can be viewed as a volume-defined water/cement (w/c) ratio. The 0.4 simulation contains 40 vol % spheres and 60 vol % void (water filled). The distance to the interface can be viewed as the thickness of the water film surrounding the aggregate. We are assuming that surface active agents such as superplasticizers reduce surface tension and the thickness of the water film. In order to emulate this difference, the distance to the interface was alternately set at 50 and 200 pixels.
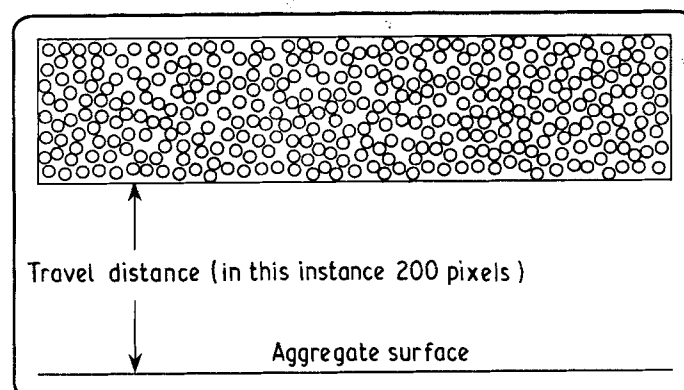

Figure 1 Computer monitor screen showing various components of the simulation. Rectangular area at top is where particles are generated at random (640 pixels × 150 pixels). Travel distance represents the water film surrounding moist aggregate particles, and the bottom line represents the aggregate surface. Monitor screen is 640 pixels wide and 350 pixels high.

Particles move towards the bottom line at random; they can move in all directions except upwards. This limitation can be considered to simulate compaction associated with any form of particle packing. It can be referred to as directed randomness [27]. Alternatively, we could have chosen another method used in some random aggregation simulations [28]: if a randomly moving particle moves too far away from the surface, it is replaced by a re-generated particle. We chose the directed randomness method because it seemed more realistic. Suspended cement particles come in contact with aggregate surfaces during mixing. The aggregate is usually wet before the addition of the cement powder. As a result there exists a discrete water film through which the cement particles must move. Most mixers use circular motion of some sort to aid in the mixing process. The large aggregate tends to pack together, held in place by centrifugal motion and gravity, the paste tends to flow around the large aggregate. We have assumed that mixing, predominantly shearing, imparts enough energy to the cement particles so that they are directed towards the aggregate surface, penetrate the water film, and eventually pack against the aggregate. Therefore, the randomness of movement simulated by the computer does not represent any specific mechanism associated with Brownian movement. Another reason for choosing directed random movement is that agglomeration of particles during ballistic movement cannot take place, even if particles are given a discrete sticking probability. Another way to form agglomerates is to select random at a pair of neighbouring particles or clusters and define them as a new cluster [29]. Once again we chose the directed random movement method because it seemed more realistic; clustering seems more appropriate for modelling nucleation and growth. It is worth noting that if no random movement is involved, simultaneous packing and sequential packing should not produce any significant differences. Our microcomputer contains only one CPU, therefore real simultaneous movement of particles is impossible. Real simultaneous movement of particles can be approached only by reducing the sequential movement of each particle to an infinitely small step.

The magnitude of particle movement is randomly selected according to a user-defined parameter called amplitude of motion. The smaller the amplitude, the more nearly simultaneously the particles move. We are correlating amplitude of motion with the energy imparted to the system by mixing. We are assuming that particles will move further relative to each other and the interfaces, if mixing is vigorous. When two particles or clusters of particles strike one another, the computer will determine if they will stick together, according to a user-defined parameter called sticking probability. A single or two different probabilities may be used for head-on and side by side collisions. In the present paper, a single value was used. Sticking probability is clearly related to the degree of flocculation which occurs in a given cement paste. We are assuming that a surface active agent such as a superplasticizer reduces interparticle attractions and thus reduces the degree of flocculation the cement particles experi-

ence. For purposes of the report, the action of such agents was emulated by varying the sticking probability from 1% (superplasticized) to 10% (non-superplasticized). When a particle/cluster reaches the interface, it will become permanently attached to the interface after 20 attempts to achieve sticking. This limitation was adopted in order to prevent infinite loops from occurring at very low sticking probabilities. Once attached, the outer boundary of the particle/cluster defines the location of the "new" interface.

The output of the program consists of a visual display of packed particles and a graph of interparticle porosity as a function of distance from the aggregate surface. Because the particles are allowed to move outside the field of view represented by the computer screen, the user can choose to view these areas and then use this information to choose a representative area within which the computer will calculate the porosity profile. By doing so, the user can avoid simulation boundary effects. In this instance, the width of the output was limited to 640 pixels.

3. Simulation results

Table I represents the starting parameters used to generate the particle packings given in Figs 2–19. To generate figures for the report, the diameter of the particle was fixed at 12 pixels and the original number of particles limited to a rectangular area 640 pixels × 150 pixels in size. A 12 pixel particle was used to aid in graphical representation. It is obvious that using smaller sized particles and a larger initial area will lead to better statistics.

Figs 2–4 represent different steps in the simulation process. Fig. 2 shows the bottom line as a flat aggregate surface (or part of a surface) and the particles generated at random in the rectangular area (no longer shown) at a very early stage of the simulation. In this instance, the rectangular area had a height of 150 pixels. The initial packing density (per cent solids in the rectangular area) was 0.4. The distance between the bottom line and the rectangular area is 200 pixels. Fig. 3 shows the intermediate stage during packing. In this instance, the sticking probability is 0.1. Some agglomeration is evident. Fig. 4 shows the final packing. Because of the agglomeration of particles, pore structures in both bulk phase and interfacial zone are, as expected, highly porous.

Comparing Figs 4 and 8, 5 and 9, 6 and 10, 7 and 11, 12 and 16, 13 and 17, 14 and 18, and 15 and 19, shows that a change in sticking probability from 0.1 to 0.01 will definitely affect the pore structure in both the bulk and the interfacial zone. For these runs, the sticking probability of head-on or side-by-side collisions were
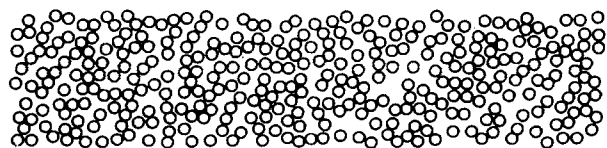
Figure 2 Initial stage of simulation. Particles have been generated and are just beginning to move towards the aggregate surface.

TABLE I Parameters used to generate particle packings

Figure number	Run number	Initial packing density	Sticking probability	Amplitude	Distance between aggregate surface and initial rectangular area
2, 3, 4	1	0.4	0.1	10	200
5	2	0.4	0.1	10	50
6	3	0.4	0.1	1	200
7	4	0.4	0.1	1	50
8	5	0.4	0.01	10	200
9	6	0.4	0.01	10	50
10	7	0.4	0.01	1	200
11	8	0.4	0.01	1	50
12	9	0.2	0.1	10	200
13	10	0.2	0.1	10	50
14	11	0.2	0.1	1	200
15	12	0.2	0.1	1	50
16	13	0.2	0.01	10	200
17	14	0.2	0.01	10	50
18	15	0.2	0.01	1	200
19	16	0.2	0.01	1	50
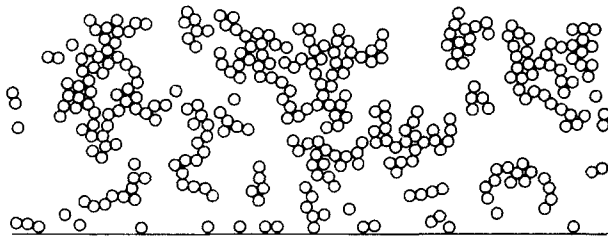
Figure 3 Intermediate stage of simulation. Some particles have settled on the aggregate surface while others are still agglomerating and moving towards it.
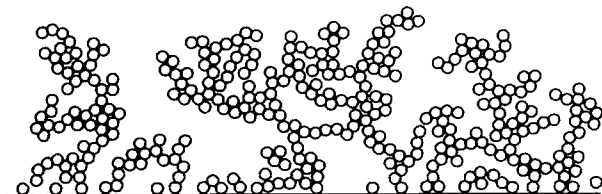
Figure 4 Final stage of simulation, Run 1. All particles are fixed on the aggregate surface. Open spaces represent initial porosity, for the most part filled with water. Simulation conditions: 0.4 packing density, 0.1 sticking probability, 10 pixels amplitude and 200 pixels to aggregate.
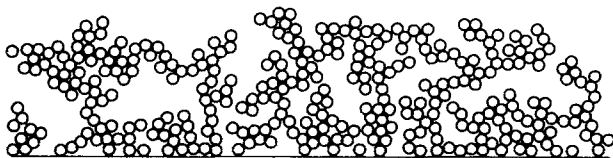
Figure 5 Final stage of simulation, Run 2. Simulation conditions: 0.4 packing density, 0.1 sticking probability, 10 pixels amplitude and 50 pixels to aggregate.
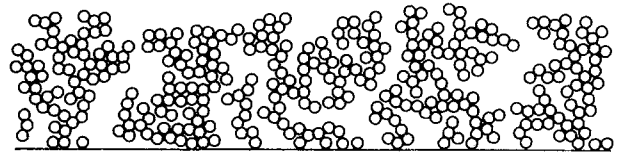

Figure 6 Final stage of simulation, Run 3. Simulation conditions: 0.4 packing density, 0.1 sticking probability, 1 pixel amplitude and 200 pixels to aggregate.
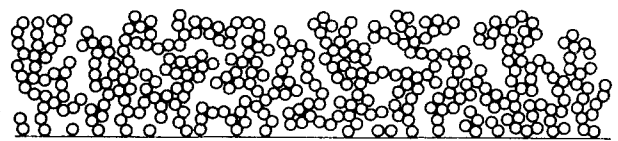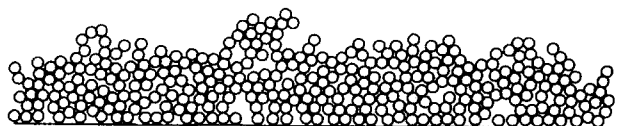

Figure 7 Final stage of simulation, Run 4. Simulation conditions: 0.4 packing density, 0.1 sticking probability, 1 pixel amplitude and 50 pixels to aggregate.

Figure 8 Final stage of simulation, Run 5. Simulation conditions: 0.4 packing density, 0.01 sticking probability, 10 pixels amplitude and 200 pixels to aggregate.

Figure 9 Final stage of simulation, Run 6. Simulation conditions: 0.4 packing density, 0.01 sticking probability, 10 pixels amplitude and 50 pixels to aggregate.

the same. As one might expect, if particles do not agglomerate, the resulting packing will be more efficient. A plot of porosity as a function of distance from the interface (measured in pixels) for Fig. 5 (0.4, 0.1, 10, 50) and Fig. 9 (0.4, 0.01, 10, 50) is given in Fig. 20. The plot is representative of the group as a whole. Simulations with lower sticking probability always result in lower porosity and better packing in the interfacial
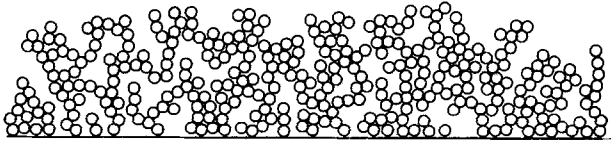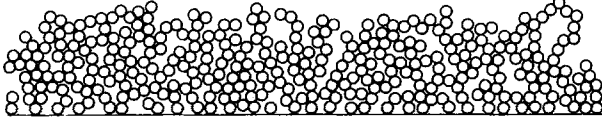
Figure 10 Final stage of simulation, Run 7. Simulation conditions: 0.4 packing density, 0.01 sticking probability, 1 pixel amplitude and 200 pixels to aggregate.

Figure 11 Final stage of simulation, Run 8. Simulation conditions: 0.4 packing density, 0.01 sticking probability, 1 pixel amplitude and 50 pixels to aggregate.
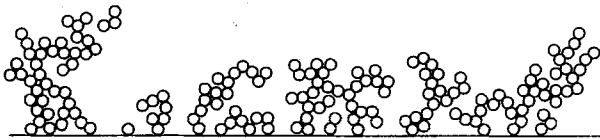

Figure 12 Final stage of simulation, Run 9. Simulation conditions: 0.2 packing density, 0.1 sticking probability, 10 pixels amplitude and 200 pixels to aggregate.
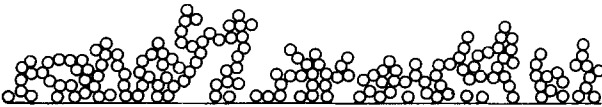

Figure 13 Final stage of simulation, Run 10. Simulation conditions: 0.2 packing density, 0.1 sticking probability, 10 pixels amplitude and 50 pixels to aggregate.

Figure 14 Final stage of simulation, Run 11. Simulation conditions: 0.2 packing density, 0.1 sticking probability, 1 pixel amplitude and 200 pixels to aggregate.
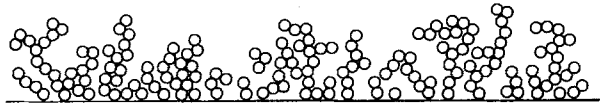

Figure 15 Final stage of simulation, Run 12. Simulation conditions: 0.2 packing density, 0.1 sticking probability, 10 pixels amplitude and 50 pixels to aggregate.

Figure 16 Final stage of simulation, Run 13. Simulation conditions: 0.2 packing density, 0.01 sticking probability, 10 pixels amplitude and 200 pixels to aggregate.

Figure 17 Final stage of simulation, Run 14. Simulation conditions: 0.2 packing density, 0.01 sticking probability, 10 pixels amplitude and 50 pixels to aggregate.

Figure 18 Final stage of simulation, Run 15. Simulation conditions: 0.2 packing density, 0.01 sticking probability, 1 pixel amplitude and 200 pixels to aggregate.
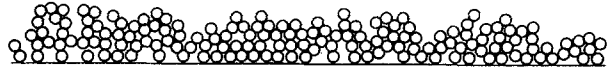

Figure 19 Final stage of simulation, Run 16. Simulation conditions: 0.2 packing density, 0.01 sticking probability, 1 pixel amplitude and 50 pixels to aggregate.
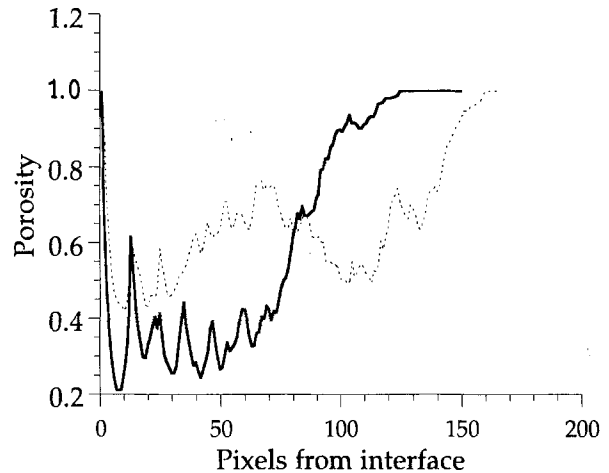

Figure 20 Effect of sticking probability (1, 10) on porosity profiles. (———) Run 6 = 1%. (----) Run 2 = 10%. Other variables were fixed (0.4, 10, 50).

zone. Very low sticking probabilities may simulate the effects of a water-reducer or any cement dispersant which reduces the degree of flocculation of the cement paste particles.

Comparing Figs 4 and 5, 6 and 7, 8 and 9, 10 and 11, 12 and 13, 14 and 15, 16 and 17 and 18 and 19, it can be seen that the distance between the aggregate surface and the rectangular area does not affect the final particle packing to any great extent. The plots given in Fig. 21 for distributions given in Fig. 6 (0.4, 0.1, 1, 200) and Fig. 7 (0.4, 0.1, 1, 50) are once again fairly typical

of the group as a whole. There is a suggestion that a smaller water film results in a less porous interface. In light of this, it would appear that the major action of a superplasticizer is the reduction of interparticle attractions, rather than the reduction of water film thickness.

Comparing Figs 4 and 6, 5 and 7, 8 and 10, 9 and 11, 12 and 14, 13 and 15, 16 and 18, and 17 and 19, one can see the effect of the amplitude on the particle packing. Amplitude of movement can be considered as a factor of the simulation which affects the degree of
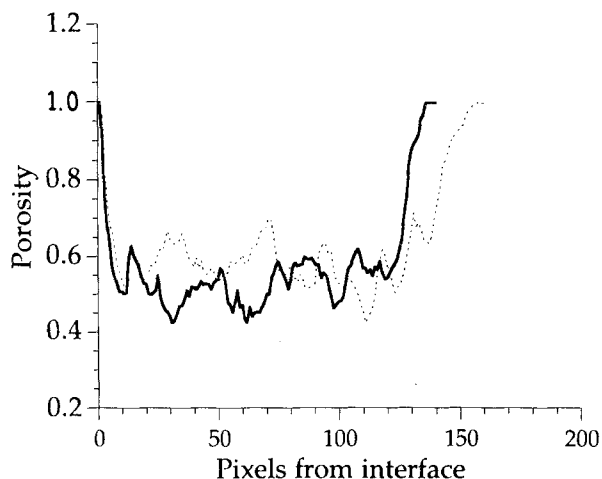
Figure 21 Effect of distance to aggregate surface (50, 200) on porosity profiles. (———) Run 4 = 50. (----) Run 3 = 200. Other variables were fixed (0.4, 0.1, 1).

(a)

Figure 22(a) Effect of amplitude of motion (1, 10) and 10% sticking probability on porosity profiles. (———) Run 3 = 1. (----) Run 1 = 10. Other variables were fixed (0.4, 200).

simultaneous movement of the particles (i.e. energy of mixing). A smaller amplitude leads to a smaller incremental step which simulates near-simultaneous movement of particles. The effect of amplitude of motion is not an entirely independent variable. It was found that sticking probability influenced the outcome of the simulations. In those runs made with a 10% sticking probability (see Fig. 22a) the simulations having a small amplitude of motion (1 pixel) exhibited better packing than their 10 pixel counterpart. In the present case, the porosity profiles of the individual simulations are very "noisy" and comparisons are hard to make. Thus, each simulation was run an additional four times and the average of five simulations were plotted against each other. This reduced the noise, eliminated overlap beyond the first particle, and confirmed the observation that Run 3 is definitely less porous than Run 1. Conversely, if the sticking probability was reduced to 1%, then the greater amplitude of motion simulation (10 pixels) exhibited better packing than its counterpart (see Fig. 22b). This is an interesting and unexpected result. A priori, it was assumed that more vigorous movement (mixing) would lead to better packing at the interface. These results suggest that the agglomeration of particles during mixing is an important phenomenon which can have a significant impact on both interface and bulk porosity. By varying the sticking probability along with the amplitude of moving the particles, one can control the degree of porosity in the packed particles.

Finally, comparing Figs 4 and 12, 5 and 13, 6 and 14, 7 and 15, 8 and 16, 9 and 17, 10 and 18, and 11 and 19, one can see that the initial packing density has little or no effect on the final packing. This is quite obviously the case when porosity profiles of particle accumulations in Fig. 4 (0.4, 0.1, 10, 200) and Fig. 12 (0.2, 0.1, 10, 200) are compared (see Fig. 23).

4. Discussion and implications

Many investigators have shown that porosity decreases as one moves away from the surface of aggregates [30]. Therefore, at least in a qualitative sense, our
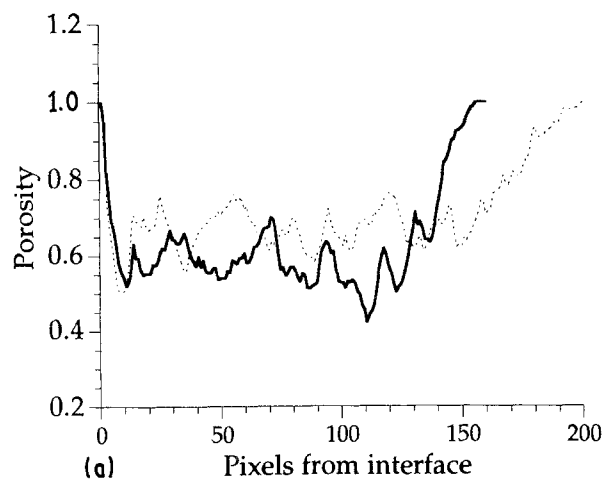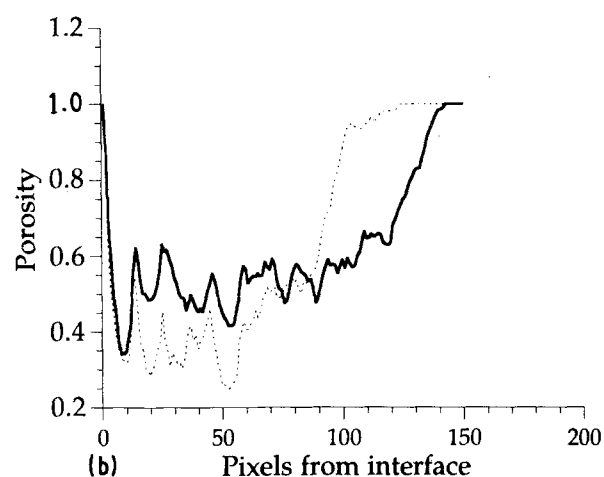

(b)

Figure 22(b) Effect of amplitude of motion (1, 10) and 1% sticking probability on porosity profiles. (———) Run 7 = 1. (---) Run 5 = 10. Other variables were fixed (0.4, 200).
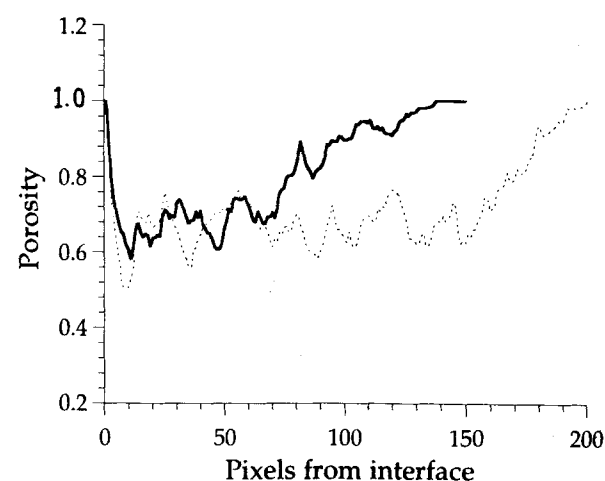

Figure 23 Effect of original particle density (0.4, 0.2) on porosity profiles. (———) Run 9 = 0.2. (---) Run 1 = 0.4. Other variables were fixed (0.1, 10, 200).

simulations confirm these observations. Porosity is seen to drop from nearly 100% directly at the interface to anywhere from 20%–60% as one moves multiples of the particle diameter (12 pixels) from the interface.

Not surprisingly, the sticking probability was found to have the single most-significant effect in determining both interface and bulk porosity. Distance to the interface (thickness of water film around the aggregate) was shown to have a lesser effect, while original particle density (w/c) had little or no effect.

What was surprising was the discovery that the amplitude of motion, which we are equating with energy of mixing, was not an independent variable. The outcome of simulations in which amplitude of mixing was varied between 1 and 10 pixels were dependent upon sticking probability. The results presented earlier seem to imply that in a highly flocculated system, gentle mixing (small amplitude of motion) would lead to a significant porosity reduction, whereas in a non-flocculated system, a more vigorous mixing would achieve similar results. If this is correct, this suggests that a non-superplasticized concrete is best mixed gently, thereby reducing interface porosity and improving mechanical performance. At the other extreme, a superplasticized concrete should apparently be mixed as vigorously as possible to reduce interface porosity. Experiments are underway to verify these predictions.

A final observation concerns the periodicity of the porosity profiles. For example, see Fig. 20. The variation in porosity is due to the formation of rudimentary layers of particles. Therefore, porosities are at a minimum at approximately one-half the particle diameter and reach a maximum at 12 pixels. If packing is less efficient, the periodicity is not as regular, and peaks and valleys are less intense. Nevertheless, this phenomenon may explain why cracks sometimes propagate a small distance away from the exact interface between paste and aggregate. Although the voids are soon filled with hydration products, the presence of such periodicity in two- or three-dimensions suggests that, next to the interface itself, these planes of high porosity could act as zones of weakness between the paste and aggregate.

5. Conclusion

Computer modelling has allowed us to carry out packing experiments under carefully controlled conditions, conditions which are impossible to examine experimentally. By using the described model, we were able to study the effect of four variables on the porosity distribution which developed across interfacial zones. In all cases, the experimentally documented decrease in porosity with distance from the surface of the aggregate was confirmed using this approach. Although the relevance of the results may be questionable, they do, in fact, point the way to new areas of research. For example, simulation results suggest that a reduction in the degree of flocculation and an increase in the energy of mixing seem to offer the best combination of variables leading to the lowest overall porosity profiles across the interfacial zone. In addition, high porosity planes have been identified, the interface itself and a series of planes which are approximately one particle diameter apart. Results are encouraging and suggest that further investigation, using both experimental research and computer simulation, may yield even deeper insight into the nature of the interfacial pore structures which develop during mixing.

References
1. R. K. McGEARY, J. Amer. Ceram. Soc. 44 (1961) 513.
2. K. RIDGWAY and K. J. TARBUCK, Brit. Chem. Engng. 12 (1967) 384.
3. D. J. CUMBERLAND and R. J. CRAWFORD, in "Handbook of Powder Technology" Vol. 6, edited by J. C. Williams and T. Allen (Elsevier, New York, 1987).
4. DO IK LEE, J. Paint Tech. 42 (1970) 579.
5. J. D. BERNAL and J. MASON, Nature 188 (1960) 910.
6. G. DAVID SCOTT, Nature 188 (1960) 908.
7. SHRP-87-C201: "Concrete Microstructure", First Quarterly Report-Year 2, April 1989.
8. PATRICK J. CREEGAN, Conc. Int. April (1990) 33.
9. EINAR L. HINRICHSEN, JEN FEDER and TORSTEIN JØSSANG, Phys. Rev. A. 41 (1990) 4199.
10. I. LEE DAVIS and ROGER G. CARTER, J. Appl. Phys. 67 (1990) 1022.
11. S. K. CHAN and K. M. NG, Chem. Engng. Commun. 48 (1986) 215.
12. J. RODRÍGUEZ, Powder Tech. 47 (1986) 25.
13. KARL HEINZ SCHÜßLER and LUTZ WALTER, Part. Charact. 3 (1986) 129.
14. H. W. LOTWICK, Stat. Comp. Simul. 15 (1982) 315.
15. M. J. POWELL, Powder Tech. 25 (1980) 45.
16. J. L. FINNEY, Mater. Sci. Engng. 23 (1976) 199.
17. WILLIAM M. VISSCHER and M. BOLSTERLI, Nature 239 (1972) 504.
18. A. J. MATHESON, J. Phys. C 7 (1974) 2569.
19. CHARLES H. BENNETT, J. Appl. Phys. 43 (1972) 2727.
20. E. M. TORY, B. H. CHURCH, M. K. TAM and M. RATNER, Can. J. Chem. Engng. 51 (1973) 484.
21. D. J. ADAMS and A. J. MATHESON, J. Chem. Phys. 56 (1972) 1989.
22. KAREN SCRIVENER, in "Materials Science of Concrete I" edited by J. Skalny, (American Ceramic Society, Westerville, OH, 1989) p. 127.
23. SIDNEY DIAMOND, in "Microstructural Development During Hydration of Cement" edited by L. Struble and P. Brown (Materials Research Society, Pittsburgh, PA, 1986). p. 21
24. EDWARD J. GARBOCZI and DALE P. BENTZ, J. Mater. Res., 6 (1991) 196.
25. G. W. GROVES, in "Microstructural Development During Hydration of Cement" edited by L. Struble and P. Brown (Materials Research Society, Pittsburgh, PA, 1986) p. 3.
26. E. M. GARTNER and J. M. GAIDIS, in "Materials Science of Concrete I" edited by J. Skalny (American Ceramic Society, Westerville, OH, 1989) p. 95.
27. R. JULLIEN, M. KOLB and R. BOTET, J. Phys. 45 (1984) 395.
28. PAUL MEAKIN, Phys. Rev. A 27 (1983) 2616.
29. W. D. BROWN and R. C. BALL, J. Phys. A. (1985) L517.
30. S. MINDESS, in "Materials Science of Concrete I" edited by J. Skalny (American Ceramic Society, Westerville, OH 1989) p. 163.