

THE EFFECTS OF CAPSULES ON SELF-HEALING EFFICIENCY IN CEMENTITIOUS MATERIALS

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Abstract

Because self-healing of cracks is able to prolong the service life of concrete structures, it has attracted plenty of attention in these years. In this research, self-healing of cracks by further hydration of unhydrated cement particles was proposed. Encapsulated water was embedded in the cement paste to promote the further hydration. When the cement matrix cracks, the capsules are broken and the water stored in the capsules is released. The further hydration is promoted when the released water accesses to the unhydrated cement particles. The cracks are expected to be healed by the hydration products. Therefore, self-healing efficiency directly depends on the amount of released water, thus on the amount of capsules hit by the cracks.

However, it is obvious that only some parts of capsules are hit by the crack when the matrix fractures. Because the amount of capsules hit by the cracks is related to the dosage of capsules mixed in the cement matrix, thus self-healing efficiency is regulated by the dosage and the size of capsules in the mixture. In order to realize the capacity of self-healing in practice, the effects of capsules on self-healing efficiency were investigated. The probability of a crack hitting capsules with a certain diameter was calculated by Monte Carlo simulations. Based on numerical studies, the self-healing efficiency as the function of the dosage of capsules was determined, taking into account the effects of the size of capsules.

1. INTRODUCTION

Cracking, caused by shrinkage and external loading, is inherent in reinforced concrete structures. The cracks in reinforced concrete structures facilitate the ingress of aggressive agents and reduce the durability of the structures. This problem can be settled in different ways and self-healing of cracks is an alternative solution [1-4]. Because self-healing of cracks is of potential to prolong the service life of concrete structures, it has attracted much attention in current years [5, 6]. For instance, mineral admixtures are used to develop self-healing concrete in Japan [7]. Bacteria are applied as self-healing agent in concrete structures in the Netherlands [8, 9]. However, the critical condition for these two methods is that extra water is

needed to penetrate into the cracks from outside environment to active the healing agent.

In this research, further hydration of unhydrated cement particles is adopted to induce self-healing of cracks. It is well known that a substantial amount of cement remains unhydrated over time due to the lack of water, especially in high performance concrete [10]. To promote further hydration, extra water is stored in capsules which are premixed in matrix. When cement matrix cracks, some capsules are broken and the water stored in the capsules is released into the cracks. The further hydration of unhydrated cement particles is promoted by the released water. The cracks are expected to be healed by the products of further hydration which are formed in the cracks. Therefore, self-healing efficiency directly depends on the amount of released water, thus on the amount of capsules hit by the cracks.

However, it is obvious that only some parts of capsules are hit by the crack when the matrix fractures. The amount of capsules hit by the crack is the function of the dosage and size of capsules premixed with concrete. Thus self-healing efficiency is regulated by the dosage and the size of capsules in the mixture. It is easy to imagine that the more capsules premixed in paste, the more water released from the broken capsules, and the higher self-healing efficiency will be achieved. Therefore, in order to realize the capacity of self-healing in practice, it is necessary to investigate the effects of the dosage and the size of capsules on self-healing efficiency.

According to previous study [11], self-healing efficiency as the function of released water was determined. This relationship as the basic of this study was reviewed in this paper. The probability of a crack hitting capsules was calculated based on Monte Carlo simulations [12]. For the calculation of hitting probability, the effects of capsule size were also taken into account. Based on numerical studies, the effects of capsules on self-healing efficiency were analyzed.

2. REVIEWS OF SELF-HEALING EFFICIENCY VERSUS THE AMOUNT OF RELEASED WATER

The relationship between self-healing efficiency and the amount of released water was determined in previous study [13]. Because this relationship is the basic of this research, it is reviewed in this section.

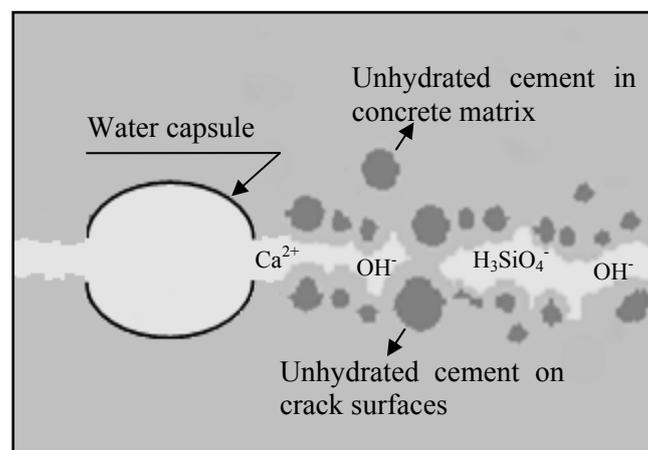


Figure 1: Schematic diagram of further hydration [13]

2.1 Mechanism of self-healing by further hydration

As shown in Figure 1, the encapsulated water is embedded in concrete matrix. Because of the low strength of capsules, the capsules are assumed to be broken when they are hit by cracks. The water stored in capsules is released immediately and the cracks are filled with water. When the unhydrated cement particles on the crack surfaces contact with water, the clinker phases of unhydrated cement dissolve instantly. Ca^{2+} begins to diffuse out from anhydrates immediately and then the silicate starts to diffuse out as well [14]. Consequently, the concentrations of various ions in the crack solution increase gradually. Once the concentrations of ions reach the equilibrium criteria for the precipitation, the further hydration products are formed in the crack. Along with the further hydration products are formed around the unhydrated cement, the rate of further hydration slows down and gradually becomes more and more diffusion-controlled [15, 16]. During this period, some parts of the ions are consumed to form the inner products while other parts of ions may diffuse into the crack solution. Therefore, the formation of healing products in the crack keeps going on, but becomes slower and slower. In addition to the unhydrated cement exposed on the crack surfaces, some ions also diffuse into the solution in the crack from the unhydrated cement embedded inside the concrete matrix (not on the crack surfaces). These ions also facilitate the formation of healing products in the crack.

What should be mentioned is that the released water in cracks will be absorbed by the concrete matrix due to capillary action. Therefore, the section of crack filled with water will decrease. However, the fact is that the precipitation of further hydration products only takes place in the section of cracks filled with water. When the water in the cracks is absorbed entirely, further hydration in cracks will stop.

2.2 Simulation of self-healing by further hydration

The processes of self-healing by further hydration mentioned above were simulated in previous study [13]. As shown in Figure 2, a crack with the size of 40 mm (length) \times 40 mm (depth) \times 10 μm (width) is supposed to pass through a capsule. Because the hydration products formed in the cement paste with low w/c ratio is very dense, some unhydrated cement particles can be also passed through by the crack. Assuming the surrounding surfaces of the cracked specimen are sealed the water evaporation will not happen and the carbonation of calcite is also prevented.

In the simulation, it was assumed that when the capsules are broken by the crack, all the water stored in the broken capsules can be released into the cracks due to the capillary action. As mentioned, the water in the crack can be absorbed by concrete matrix. The amount of water existing in the crack can be calculated with a water transport model, which is based on mass balance [17-19].

The further hydration processes in water-bearing section of the cracks were simulated in micro level. A tiny square with the size of 100 μm \times 100 μm (excluding the crack width) as simulation system from the water-bearing section of crack is shown in Figure 2. The distribution of unhydrated cement particles was simulated by HYMOSTRUC3D [15, 20, 21]. The tiny square was discretized into micro-pixels with the size of 2 μm \times 2 μm . The ion concentrations in each micro-pixel were calculated by the ion diffusion model based on Fick's law. Meanwhile, a thermodynamics model based on chemistry equilibrium, mass balance and ion charge balance was utilized to simulate the further hydration taking place in the micro-pixels. At each time step, the ion concentrations calculated by the diffusion model in each

micro-pixel were input into the thermodynamics model. Through the thermodynamics model, the amount of further hydration products was calculated, as well as the ion concentrations after the chemical reaction. The outputs of concentration from the thermodynamics model were input into the diffusion model again as the initial conditions for the next step of calculation. The condensed flowchart of the model for further hydration is shown in Figure 3. The self-healing efficiency, defined as the volume ratio of the further hydration products to the crack, can be determined by coupling the water transport and further hydration of cement particles.

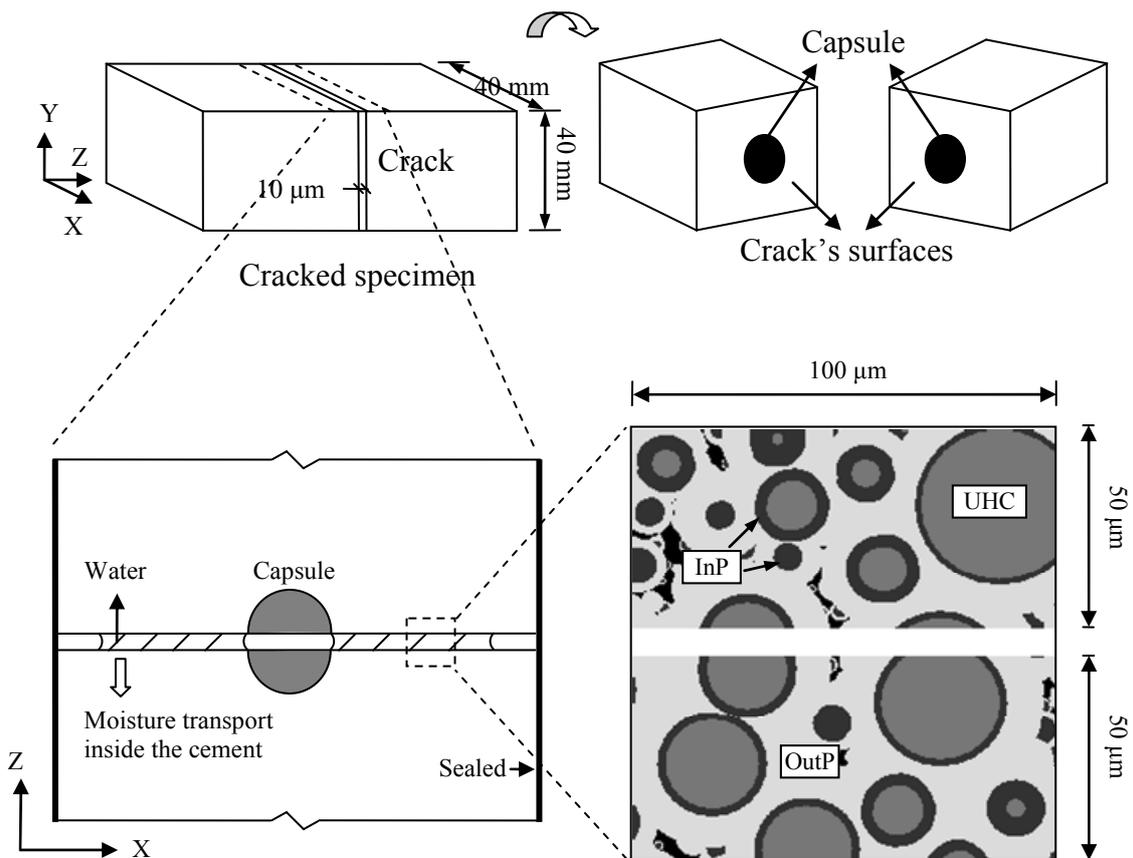


Figure 2: Schematic diagram of modeling system for further hydration (InP represents inner products, OutP represents out products, UHC represents unhydrated cement particles) [13]

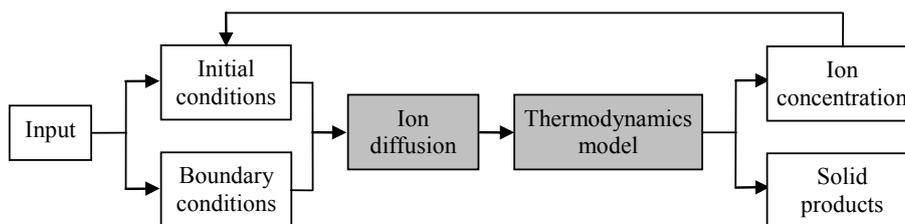


Figure 3: Flowchart of the model for further hydration [13]

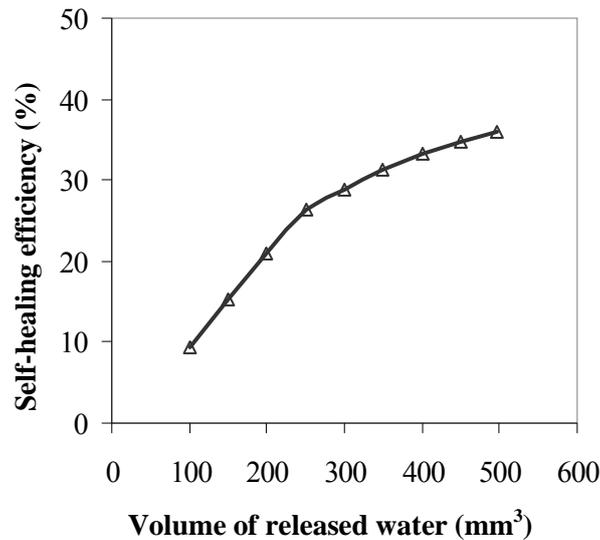


Figure 4: Self-healing efficiency by providing different amount of extra water [13]

2.3 Self-healing efficiency versus amount of available water

Based on the method in Section 2.2, the relationship between self-healing efficiency and the amount of water released from broken capsules was determined. As shown in Figure 4, self-healing efficiency rises with the increase of released water at two different rates. When 100 mm³ of water is provided into the crack, of which the size is 40 mm (length) × 40 mm (depth) × 10 μm (width), the final self-healing efficiency is about 9.5%. While the broken capsules provide 150 mm³ of water, the final self-healing efficiency increases to 15.3%. With this significant rate, the final self-healing efficiency rises to 22.9% when the extra water increases to 250 mm³. However, the increasing rate of healing efficiency slows down after this point. The reason is that when the released water contacts with the unhydrated cement on the crack surfaces, further hydration products increase dramatically. Along with the further hydration products formed around the unhydrated cement, further hydration slows down gradually. Therefore, the increasing rate of healing efficiency to the amount of extra water becomes slow when the water is more than 250 mm³.

3. PROBABILITY OF A CRACK HITTING CAPSULES

As discussed in Section 2, self-healing efficiency depends on the amount of released water from the broken capsules. In the simulation, it is assumed that the capsules can be broken when it is hit by the crack. It is easy to imagine that only some parts of capsules are hit by cracks since the capsules randomly distribute in the whole structure. The hitting probability is dominated by the dosage, the size and the shape of capsules. In this study, all the capsules are supposed to be sphere. Monte Carlo simulations were used to calculate the hitting probability, in which the effect of capsule size was also taken into account.

3.1 Principles of the computer model

Corresponding to the simulation in Section 2, the modeling system here is a beam with the size of 40 mm × 40 mm × 160 mm. As shown in Figure 5, all capsules with identical radius are uniformly dispersed inside the beam and do not overlap or contact with each other. In

addition, the capsules can not cross with the surfaces of the beam.

In this study, the cement paste is simplified as homogeneous material. The interface transition zone between cement paste and capsules is assumed to be strong enough to make the crack pass through the capsules. In this case, the crack is planar and can be simplified as a plane. Therefore, the hitting probability is equal to the probability of the capsules' centers dispersing inside the "influence zone" of the planar crack, which is shown in Figure 5(b). To obtain the probability of capsules centers dispersing inside the "influence zone" of the planar crack, 1000 random experiments were carried out. Statistic analysis on the amount of capsules passed through by the planar crack was performed. According to the statistic analysis, 1000 experiments can guarantee that the average amount of capsules hit by the crack is within 10% of the true value in a 95% degree of confidence.

3.2 Results and discussion

The probability of the planar crack hitting different amounts of capsules is shown in Figure 6. When the dosage of capsules is 5% and the diameter of the capsules is 5 mm, the probability is 1 for the event that 0.5% of the capsules in the sample are hit by the crack. When the fraction of capsules broken by the crack increases, the corresponding probability decreases. It is impossible for the crack to break all the capsules mixed in the sample. As shown in Figure 6, the probability is almost 0 for the even that more than 6% of the capsules in the sample are hit by the planar crack. In other cases of diameter, the hitting probability varies in similar tendency.

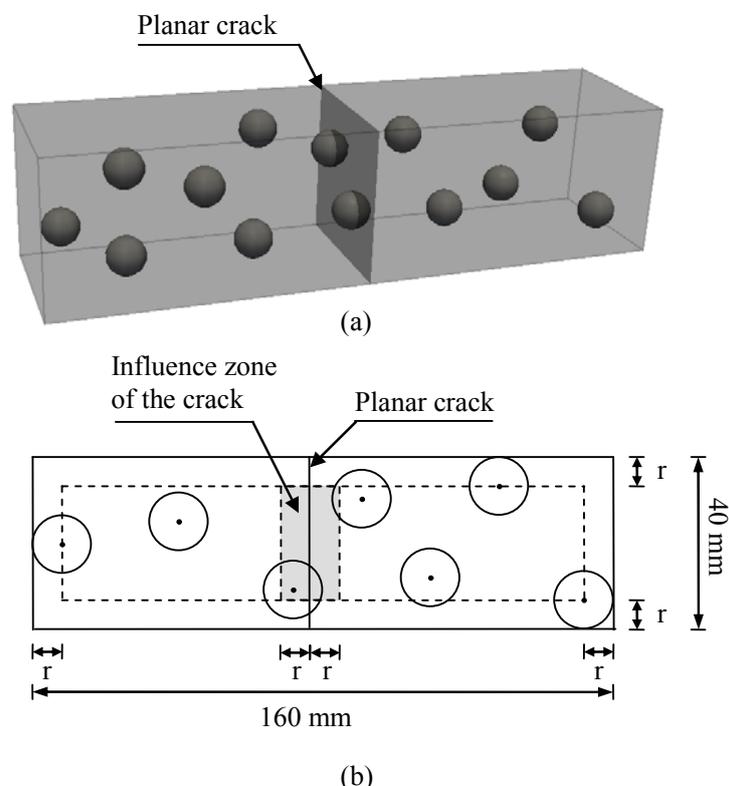


Figure 5: Schematic diagram of a planar crack hitting capsules (a); planform for the capsule distribution in the sample and the influence zone of the planar crack (b)

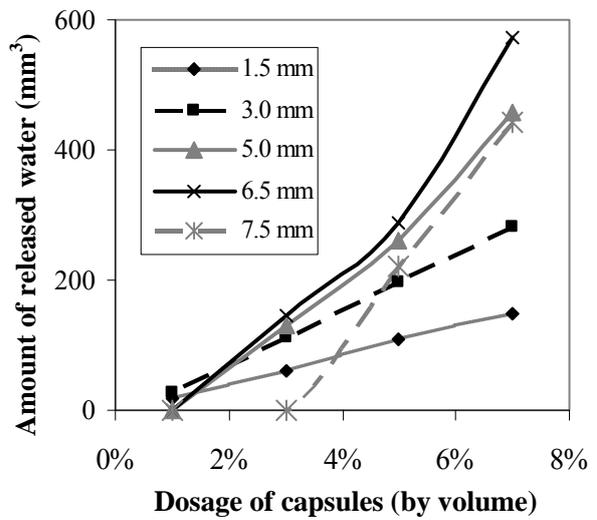
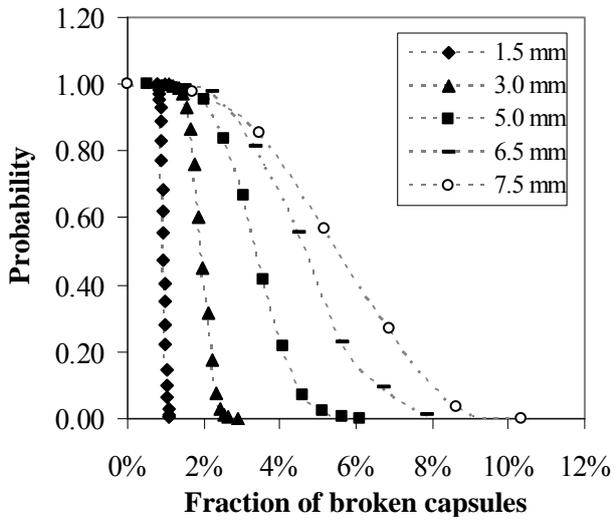


Figure 6: Probability of a crack hitting capsules (The dosage of capsules is 5%.)

Figure 7: Amount of water released from broken capsule (The degree of confidence is 95%.)

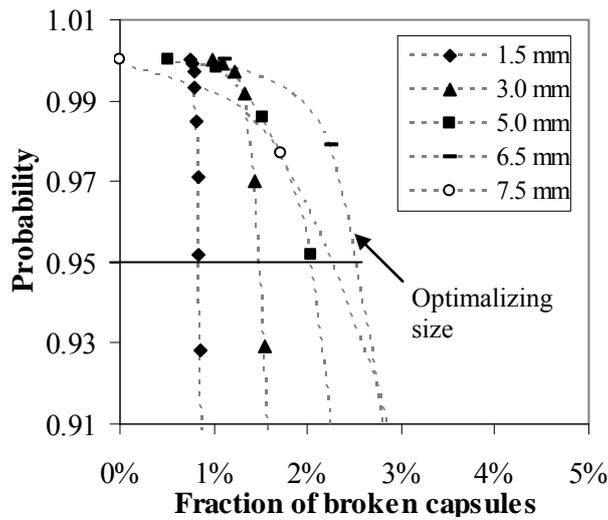


Figure 8: Probability of a crack hitting capsules with different size (Volume fraction of capsules mixed: 5%)

As mentioned before, because of the low strength of the capsules, the capsules are assumed to be broken when they are hit by the crack and the water is released into the crack from the broken capsules. The amount of released water, corresponding to different dosage of capsules, is shown in Figure 7. For this calculation, the degree of confidence is 95% (the probability is 0.95). It is found that the amount of released water is influenced by the size of capsules. When the size of capsules is small enough, i.e. 1.5 mm and 3 m, the amount of released water linearly increases with the increase of capsules. This increasing tendency varies when the size of capsules ranges from 5 mm to 7.5 mm. From Figure 7, it can be learned that, concerning the maximum amount of released water, there is an optimizing size of capsules in each case of

dosage of capsules. The optimizing size of capsules is 3.0 mm when the dosage of capsules is 1%. In comparison, the optimizing size of capsules increases to 6.5 mm while the dosage of capsules in the sample is 3%, 5% and 7% respectively. This suggestion is also demonstrated in Figure 8. When the dosage of capsules mixed in the sample is 5%, the fraction of broken capsules varies with the size of capsules while the probability is at the same level. In this study, the degree of confidence is expected to be 95%, which means that the probability of the even should be 0.95. With this probability, the fraction of capsules broken by the crack ranges from 0.84% to 2.3% when the diameter of capsules changes from 1.5 mm to 7.5 mm. What should be mentioned is that when the size of capsules is 6.5 mm, the amount of broken capsules is largest.

From this modeling, the amount of released water as the function of the dosage of capsules premixed is determined, which is essential to self-healing efficiency by further hydration. Moreover, the optimizing capsule sizes for different dosage of capsules premixed are suggested. This optimization on capsule size can significantly improve self-healing of cracks by further hydration in cementitious materials.

4. THE EFFECTS OF CAPSULES ON SELF-HEALING EFFICIENCY

Based on Figure 4 and 8, the relationship between self-healing efficiency and the dosage of capsules with different size can be determined, which is shown in Figure 9. It is clear that the self-healing efficiency increases with the increase of capsules. As discussed in Section 3.2, the amount of water released from the broken capsules is the largest when the diameter of capsules is 6.5 mm (The dosage of capsules is more than 3%). Therefore, as shown in Figure 9, the self-healing efficiency is the highest when the capsules size is 6.5 mm and the dosage of capsules is more than 3%.

However, according to the previous study, the strength of the matrix will decrease when liquid capsules are added into the matrix because of the low strength of liquid capsules [22]. Therefore, it is necessary to quantify the negative effects of capsules on mechanical properties in the future study.

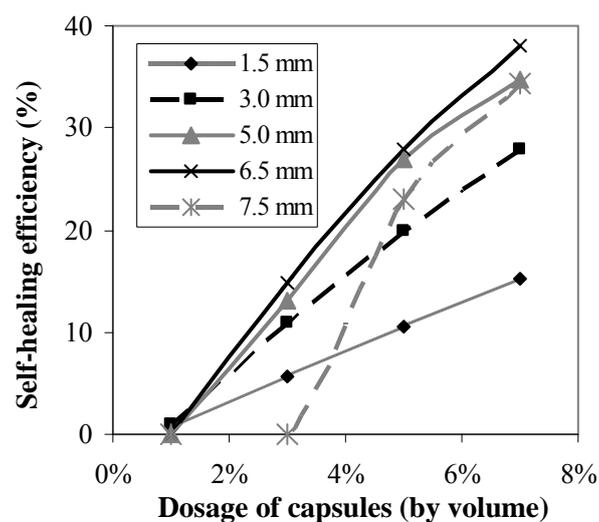


Figure 9: The self-healing efficiency with different amount of capsules

5. CONCLUSIONS

In this study, self-healing of cracks is induced by further hydration of unhydrated cement particles. Extra water for the promotion of further hydration is stored in capsules which are premixed in the matrix. When the cement matrix cracks, the capsules are broken by the cracks and the water stored in the capsules is released into the cracks. Further hydration of unhydrated cement particles is promoted by the released water. The cracks are expected to be healed by the hydration products.

The effects of the dosage and size of capsules on self-healing and mechanical properties in cementitious materials were investigated in this paper. The probability of a crack hitting capsules was calculated. By this way, the relationship between the amount of released water and the dosage of capsules mixed in the sample was determined. Besides that, the effects of the capsule size on the amount of released water were also explored.

From the results, it can be learned that the increase rate of the amount of released water to the dosage of capsules changes with the size of capsules. Concerning the maximum amount of released water, the optimizing size of capsules is 6.5 mm while the dosage of capsules is 3%, 5% and 7% respectively. Based on the relationship between self-healing efficiency and the amount of released water from the broken capsules, self-healing efficiency as the function of the dosage of capsules mixed in the matrix was determined.

ACKNOWLEDGMENTS

The authors would like to thank the China Scholarship Council (CSC) for the financial support for this work. All reviews' constructive comments and suggestions are gratefully appreciated.

REFERENCES

- [1] Evardsen, C., 'Water permeability and autogenous healing of cracks in concrete', *ACI Materials Journal* 96(4) (1999) 448-454.
- [2] Reinhardt, H.-W. and Jooss, M., 'Permeability and self-healing of cracked concrete as a function of temperature and crack width', *Cement and Concrete Research* 33(7) (2003) 981-985.
- [3] Granger, S., Loukili, A., Pijaudier-Cabot, G., and Chanvillard, G., 'Experimental characterization of the self-healing of cracks in an ultra high performance cementitious material: Mechanical tests and acoustic emission analysis', *Cement and Concrete Research* 37(4) (2007) 519-527.
- [4] Daisuke Homma, H.M.a.T.N., 'Self-healing capability of fibre reinforced cementitious composites', *Journal of Advanced Concrete Technology* 7(2) (2009) 217-228.
- [5] Yang, Y., Lepech, M.D., Yang, E.-H., and Li, V.C., 'Autogenous healing of engineered cementitious composites under wet-dry cycles', *Cement and Concrete Research* 39(5) (2009) 382-390.
- [6] Granger, S., Pijaudier Cabot, G., Loukili, A., Marlot, D., and Lenain, J.C., 'Monitoring of cracking and healing in an ultra high performance cementitious material using the time reversal technique', *Cement and Concrete Research* 39(4) (2009) 296-302.
- [7] Ahn, T.H. and Kish, T., 'Crack self-healing behavior of cementitious composites incorporating various mineral admixtures', *Journal of Advanced Concrete Technology* 8(2) (2010) 16.
- [8] Jonkers, H.M., Thijssen, A., Muyzer, G., Copuroglu, O., and Schlangen, E., 'Application of bacteria as self-healing agent for the development of sustainable concrete', *Ecological Engineering* 36(2) (2010) 230-235.
- [9] Wiktor, V. and Jonkers, H.M., 'Quantification of crack-healing in novel bacteria-based self-healing concrete', *Cement and Concrete Composites* 33(7) (2011) 763-770.

- [10] Van Tuan, N., Ye, G., van Breugel, K., and Copuroglu, O., 'Hydration and microstructure of ultra high performance concrete incorporating rice husk ash', *Cement and Concrete Research* 41(11)1104-1111.
- [11] Huang, H. and Ye, G., 'Simulation of self-healing by further hydration in cementitious materials', *Cement and Concrete Composites* 34(4) (2012) 460-467.
- [12] Mookhoek, S.D., Fischer, H.R., and Zwaag, S.v.d., 'A numerical study into the effects of elongated capsules on the healing efficiency of liquid-based systems', *Computational Materials Science* 47(2) (2009) 506-511.
- [13] Huang, H. and Ye, G., 'Simulation of self-healing by further hydration in cementitious materials of self-healing by further hydration in cementitious materials', *Cement and Concrete Composites* 34(4) (2012).
- [14] Dent Glasser, L.S., Lachowski, E.E., Mohan, K., and Taylor, H.F.W., 'A multi-method study of c3s hydration', *Cement and Concrete Research* 8(6) (1978) 733-739.
- [15] van Breugel, K., 'Simulation of hydration and formation of structure in hardening cement-based materials', PhD thesis, (Delft University of Technology, 1991)
- [16] Taylor, H.F.W., 'Cement chemistry', (Thomas Telford Publishing, London, 1997).
- [17] Maekawa, K., Chaube, R. and Kishi, T., 'Modeling of concrete performance: Hydration, microstructure and mass transport', (E & FN Spon, London, 1999).
- [18] Cerny, R. and Rovnanikova, P., 'Transport process in concrete', (Taylor & Francis, London, 2002).
- [19] Huang, H., Ye, G., and van Breugel, K., 'Numerical simulation on moisture transport in cracked cement-based materials in view of self-healing of crack', *Journal of Wuhan University of Technology--Materials Science Edition* 25(6) (2010) 1077-1081.
- [20] Koenders, E.A.B., 'Simulation of volume changes in hardening cement-based materials', PhD thesis, (Delft University of Technology, 1997)
- [21] Ye, G., 'Experimental study and numerical simulation of the development of the microstructure and permeability of cementitious materials', PhD thesis, (Delft University of Technology, 2003)
- [22] Hua, X., 'Self-healing of engineered cementitious composites (ECC) in concrete repair system', (2010).