Journal of Ceramic Processing Research. Vol. 16, Special. 1, pp. s14~s21 (2015)

J O U R N A L O F
Ceramic
Processing Research

Intelligent resilience of cementitious materials for marine infrastructures

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In this paper, a novel intelligent resilience system of cementitious materials for marine infrastructures developed recently at Shenzhen University is introduced. The aim of this system is to provide intelligent resilience against attacks of the marine environment on infrastructures made of cement-based materials, resulting in infrastructures with durability properties that far exceed those of conventional ones. Starting from the principles of intelligent resilience, the logic line of development of such a system is followed. Fundamental terms related to the resilience concept are discussed. On-going researches on material systems, design procedures and numerical models will be highlighted. The major challenges and further development concerning the intelligent resilience in cementitious materials will be addressed.

Key words: Intelligent resilience, Cementitious materials, Marine infrastructures, Durability

Introduction

Due to the shortage of resources and the increase in population, it is inevitable for human beings to seek the solutions in the oceans or their surroundings in order to improve living conditions and to keep pace with the increase of population. In the construction world the 21st century will be known as the century of cement based materials in the oceans.

Among the mostly available structural materials, cementitious materials, together with steel reinforcement, have become the most commonly used material for building marine structures because of the economic and widespread availability of its constituents, its versatility, its durability, and its adaptability.

However, it is well know that the marine environment is highly inhospitable for commonly used materials of construction, including reinforced cementitious materials. Over decades, numerous performance degradations have been observed in marine infrastructures due to the attack of corrosive ions, gases and other type of aggressive actions in the marine environment.

Expensive repair and maintenance have to be in place in order to keep the targeted performance and service life of infrastructures. It has been estimated that the annual cost of repair of concrete structures in Europe is in excess of $20 billion [5]. In China the loss due to corrosion of concrete reinforcement is about 250 billion RMB per year, with the rate of loss increasing by about 10% annually. For some cases, repair or demolish of degraded infrastructures are even out of question either due to economic reasons or something concerning the sustainability [4]. Therefore, the durability of construction materials is of more concern to civil engineers than ever before.

Recent years the so-called self-healing materials have been exploited in civil engineering, which have the built-in capability to repair structural damage autogenously or with the minimal help of an external stimulus [6, 16]. By application of this new type of advanced material in civil engineering can reduce or eliminate the necessity of repairing and long-term maintenance, resulting in durable and sustainable marine infrastructures.

In this paper, a novel intelligent resilience system of cementitious materials for marine infrastructures developed recently at Shenzhen University is introduced. The aim of this system is to provide intelligent resilience against attacks of the marine environment on infrastructures made of cement-based materials, resulting in infrastructures with durability properties that far exceed those of conventional ones. Starting from the principles of intelligent resilience, the logic line of development of such a system is followed. Fundamental terms related to the resilience concept are discussed. On-going researches on material systems, design procedures and numerical models will be highlighted. The major challenges and further development concerning the intelligent resilience in cementitious materials will be addressed.

Principles of Intelligent Resilience

Classification of resilience

It is well known that cementitious materials are quasi-brittle materials, strong in compression but relatively weak in tension. To compensate this sort of weakness steel reinforcement is installed. Passive

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Fig. 1. Illustration of resilience classification.

reinforcement is activated as soon as the cracks criss-cross rebar's. It has to be emphasized that the formation of cracks is regarded as an inherent feature of reinforced cementitious materials. Although at material level, cracks are considered as performance failure, at element level and at structural level, however, this is not considered as damage or failure and cracking as such does not indicate a safety problem as far as the load-bearing performance is concerned.

On the other hand, the degradation of performances at a material level can lead to two type of consequences, which have direct and indirect influences on the performances at element and structural level, i.e. degradation of material performance due to the transportation of harmful agents in cementitious materials, resulting in deterioration of mechanical properties and the corrosion of steel reinforcement, which will in turn affect the load-bearing capacity of the structure. Probably the most fundamental impact of microcracks on the performance at material level is the contribution to the permeability of cementitious materials by means of the formation of a continuous channel to be convenient for the transportation of harmful substances inside materials.

As described above, resilience of a performance can be classified as the following: material damage is related to healing and degradation of functionality is related to recovery (see Fig. 1).

Strategy of the intelligent resilience system for cementitious materials

An intelligent resilience system can be characterized by the following four aspects: container, healing material, trigger, healing process. Generally this is an independent system embedded in the targeted body. However, if it is designed as a hybrid system, then it can be regarded as one material system [16].

Normally the healing material needs to be sheltered to avoid the pre-mature damage or functionality. To fulfill this type of requirements a container is quite necessary. The fundamental features of such a container should be the compatibility with both healing material and the targeted body. It has to be mechanically strong but not too extreme in order to facilitate the trigger mechanism. Sometimes it has to be water tight or impermeable for any type of media. The other has to be living-friendly (e.g. no harmful effect on bacteria). Its size, surface character are in turn decisive to the resilience efficiency at different scales.

Various materials can be chosen as healing materials, depending on the to-be healed performance. Currently organic materials (such as polymers) are mostly used for this purpose, mainly due to its fluidity and quick solidification. Additionally, the repaired material is better to be organic for the sake of compatibility. For the in-organic materials, such as cementitious materials, the interface problem (in special durability) is always troublesome. Therefore, the calcium precipitation created by bacteria seems to be very desirable for the healing of cementitious materials. Hydrated in-organic materials could also be options if the mobility and rapid hydration issues could be solved.

For an intelligent resilience system a trigger is an indispensable element. Trigger has to be set up on the basis of certain criteria. As the targeted criteria have been satisfied the trigger system is excited and the resilience system will be turned on. Basically a trigger can be classified as physical or chemical trigger, depending on the exciting characteristics. The mostly told physical trigger is the stress-induced crack in a material. Other physical phenomenon, such as temperature or vibration can be used as a trigger. There are a wide range of possibilities as far as the chemical trigger is concerned. For a cementitious material, in combination with its potential degradation mechanisms, the possible chemical trigger could be harmful ion, such as chloride or sulphate, or pH value due to CO_2 induced carbonation.

Depending on the class of resilience (self-healing or self-recovery), healing process can follow quite different lines. For damage related healing disintegrated surface has to be joined together by healing agent, whereas for recovery related healing, the previous status has to be re-stored by means of reducing of harmful ion concentration of increasing pH value.

At the end, the total resilience system has to be evaluated by means of efficient ways to verify its feasibility and applicability.

On-going Researches at Shenzhen University

Pioneer work since 2008

Since 2008 attempts had been made to introduce a novel microcapsule based self-healing system into cementitious composites at Shenzhen University [9]. The first challenge concerning the microcapsule technology is to balance the fundamental requirements, namely, a microcapsule should be strong enough in order to resist the mechanical impact without breaking during making of cementitious materials, however, it must not be too strong for a physical trigger working effectively. The second challenge is to find the suitable

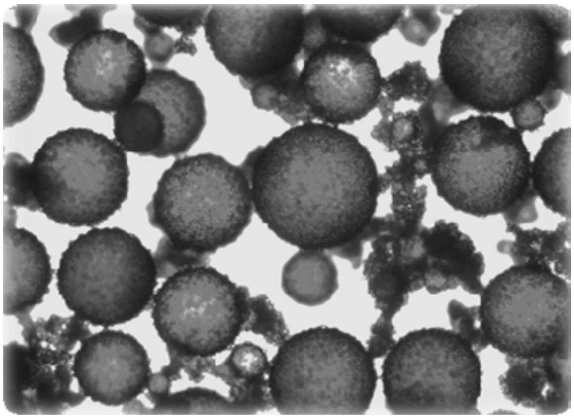

Fig. 2. Microcapsule after encapsulation.

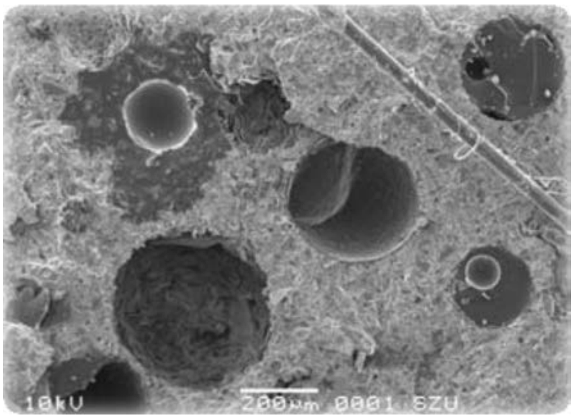

Fig. 3. Broken surface of cementitious composites with microcapsules.

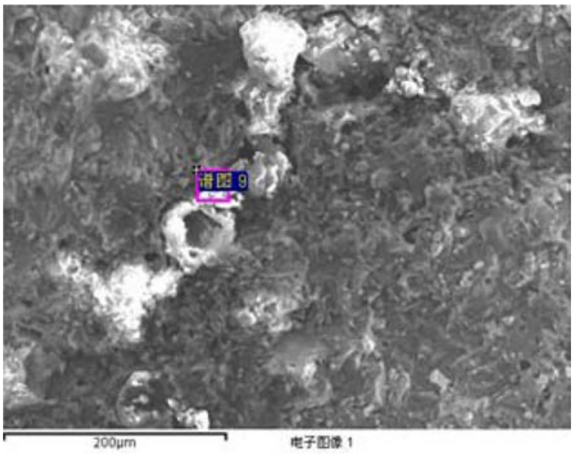

Fig. 4. Healing materials in cracks after solidification.

healing material with good fluidity and low viscosity, being able to solidify efficiently as the target position is reached.

The urea formaldehyde resin was used for the wall of microcapsule, and bisphenol-an epoxy resin E-51 diluted by n-butyl glycidy ether (BGE) was adopted as the healing-agent inside the microcapsule. A combination of latent curing agent MC120D and tetraethylene penamine (TEPA)-a type of liquid curing agent functioning at

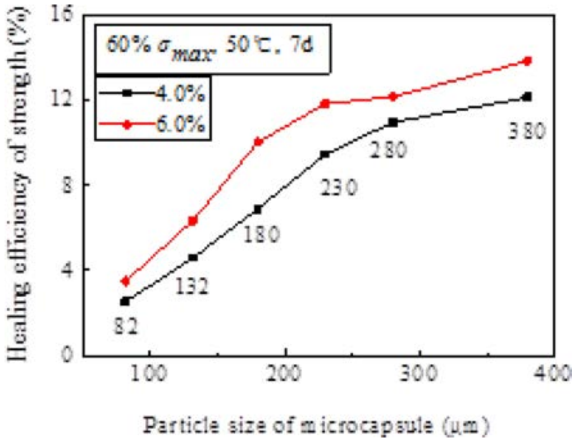

Fig. 5. Healing efficiency of strength in relation to the size and percentage of microcapsules.

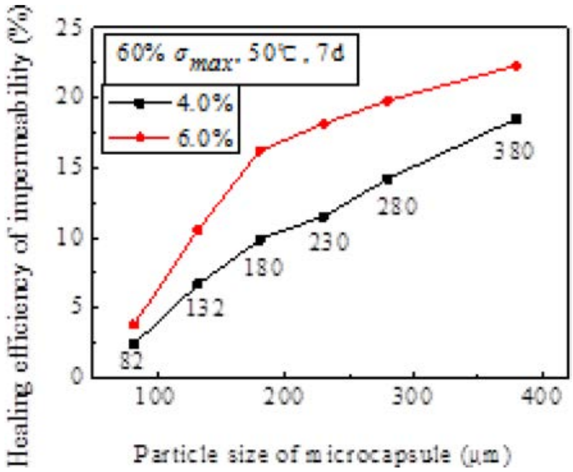

Fig. 6. Healing efficiency of impermeability in relation to the size and percentage of microcapsules.

normal temperature was used for curing the healing product. Results showed that the microcapsule obtained with the adopted production process can be used for the self-healing system in the cementitious materials. Fig. 2 shows the obtained microcapsule after encapsulation.

The feasibility of the adopted methods for making microcapsule and encapsulation was further proved by broken the cementitious composites after hardening. It could be clearly seen that the microcapsules remain undamaged during the producing of cementitious composites (see Fig. 3). The trigger seems to be working (part of microcapsules are broken).

The healing mechanism is further demonstrated by examine the picture in Fig. 4. The healing materials fill in the cracks and solidify afterwards.

The healing efficiency with respect to the mechanical and permeability performance were evaluated by experiments, respectively [12, 8]. Several important parameters had been studied, such as the size and dosage percentage of microcapsules, loading level, temperature, etc. The healing of the flexure tensile strength of cementitious materials is shown in Fig. 5. In addition, the RCM (Rapid Chloride Migration) test was adopted for the evaluation of the recovery of impermeability performance (see Fig. 6).

It is clearly shown that the attempts to introduce a novel self-healing system in cementitious composites at Shenzhen University are successful. This encouraged the research team to further explore a more comprehensive system for the marine infrastructures.

A microcapsule based integrated system

On the basis of our successful experiences and the team with strong knowledge and skill of making various types of microcapsules, a comprehensive and integrated system was proposed and several cohesive research projects from Nature Science Foundation of China were obtained recently.

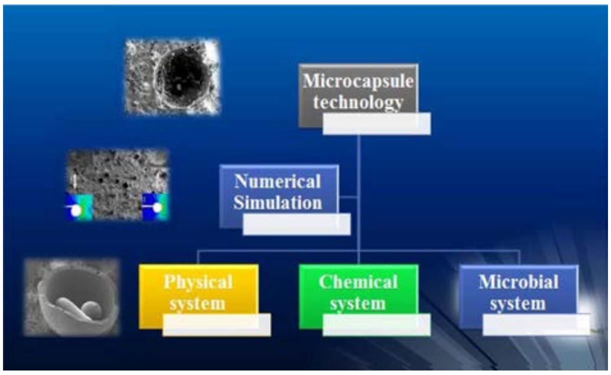

Fig. 7. A microcapsule based intelligent resilience system in cementitious materials.

The Strategy of our research is based on the micro-capsule technology. In another words, the container of resilience system is fixed on the microcapsule, however, the type of materials of microcapsules could be essentially different (e.g. organic or in-organic, life-friendly, water-proof, etc.). As far as the healing-agent is concerned, it could be in a large range of options, from organic, bacteria to in-organic materials. Thirdly, not only physical trigger (mechanical trigger) is further explored, the so called chemical trigger is largely drawn major attention in our current researches. This is in turn to be related to the resilience principle, namely, healing and recovery at a multi-scale. As a result, three interlinked systems have been formed (Fig. 7):

Physical system (organic or in-organic healing agent, physical trigger, self-healing at micro or meso level)

Chemical system (organic or in-organic healing agent, chemical trigger, self-recovery at multi scale)

Microbial system (bacteria as healing agent supplier, physical trigger, self-recovery at meso or macro level)

Current progress

Microcapsule technology

It is clear that the microcapsule technology is essential to obtain a successful self-resilience system. Only to be able produce microcapsules is certainly not sufficient.

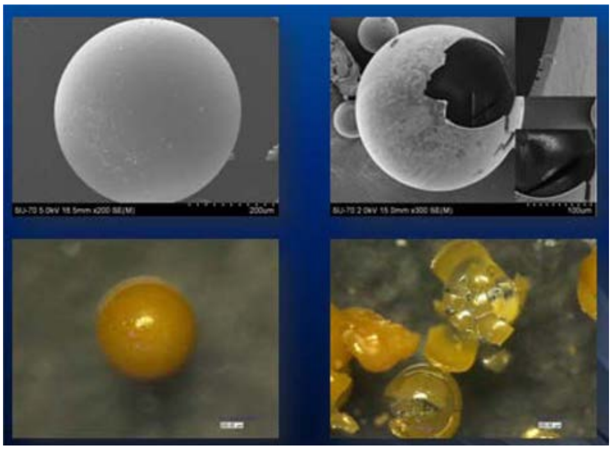

Fig. 8. A microcapsule production of fully controlled size, shell thickness and surface texture.

The challenges relate to the control of size, surface and shell thickness of an individual microcapsule in general, but also to the trigger mechanism and healing mechanism relevant issues, such as type of shell materials, type of materials to be encapsulated and so on. Fig. 8 shows the example of individual microcapsule, of which the size, shell thickness and the texture of surface can be fully controlled [13-15].

For an attempt to enable one type of chemical trigger, microcapsules are firstly produced with sodium monofluorophosphate and microcrystalline cellulose, which are mixed into Polysorbate 80. Then the small spherical particles are molded by extrusion method. After that, the microcapsules are fabricated through the spray drying method [1-3]. Fig. 9 shows the clear trigger mechanism, in this case, being pH value sensitive (which could be related to the carbonation

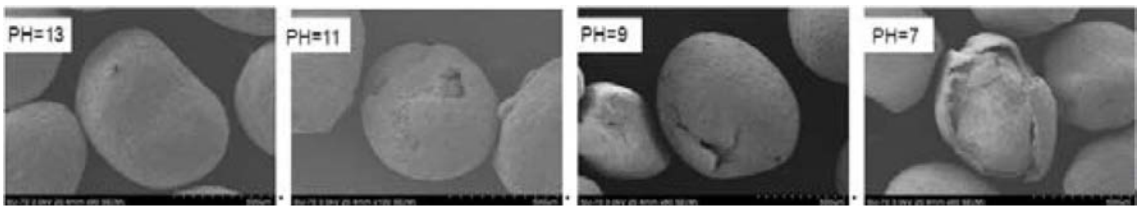

Fig. 9. Microcapsule sensitive to the variation of pH values.

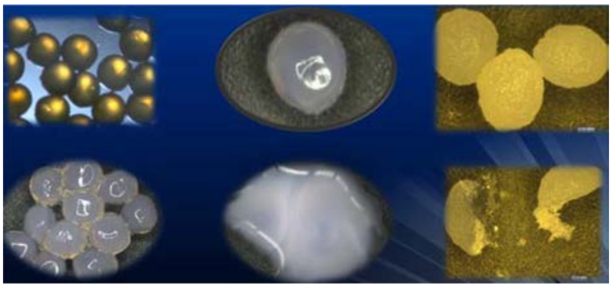

Fig. 10. Chloride-triggered microcapsule (several examples).

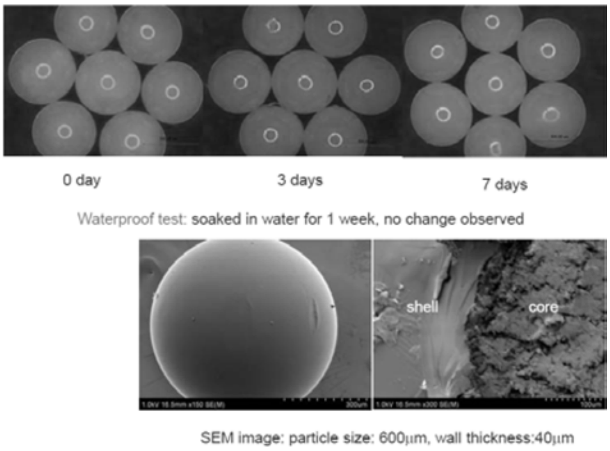

Fig. 11. Water-proof microcapsules for encapsulation of bacteria.

behavior in cementitious materials).

A novel idea related to the performance self-recovery was firstly proposed and patented by Shenzhen University. By means of a chemical trigger a self-resilience system based on the microcapsule technology has been developed, where the capacity to resist the penetration of harmful agent into cementitious materials will be restored. As the concentration of this harmful agent reaches to a certain level the microcapsule will be broken and the healing material inside the microcapsule will take actions to 'eat-up' the harmful agent. Remarkable progress has been made recently. Up to now, there are five to six different type of solutions and further optimization is needed before this can be fully implemented in the cementitious materials. Fig. 10 shows several examples of this type of chloride-triggered microcapsules [10].

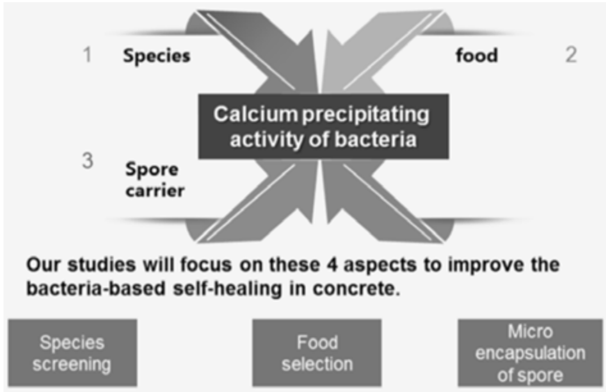

Fig. 12. Several key issues for a feasible microbial self-healing system.

Another example is to make microcapsule biocompatible and water-proof, especially for the microbial system. The selected shell material and manufacturing process cannot be harmful for bacteria. During the dormant period the bacteria cannot contact with water. Therefore, the shell of microcapsule has to be water-proof (see Fig. 11).

Microbial self-healing system

To obtain the feasible microbial self-healing system, several essential issues have to be solved (see Fig. 12). The first step is to select the most efficient bacteria species. A high through-put procedure was established for the determination of calcium precipitating activity (CPA) of bacteria in order to obtain a high-efficiency calcium-precipitating bacterium. Fig. 13 shows that Bacillus sp.H4 is the most promising species by means

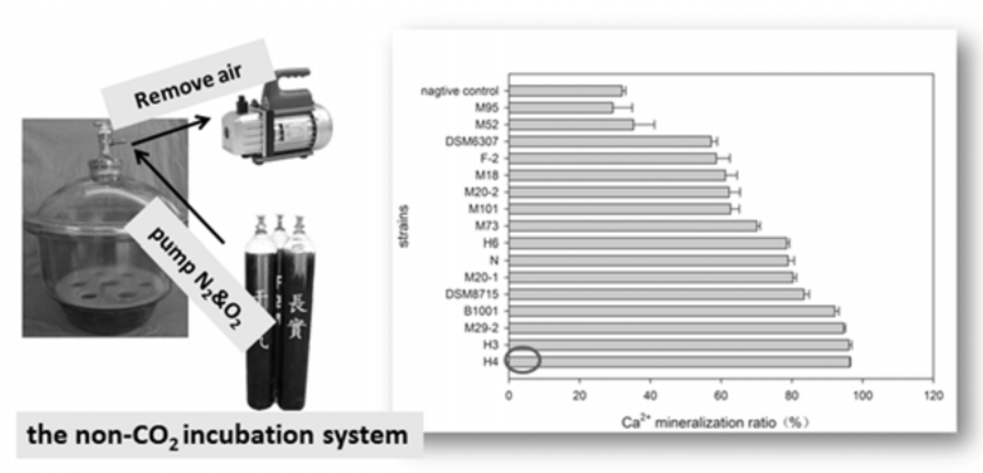

Fig. 13. The screening of high-efficiency Ca-mineralizing bacteria.

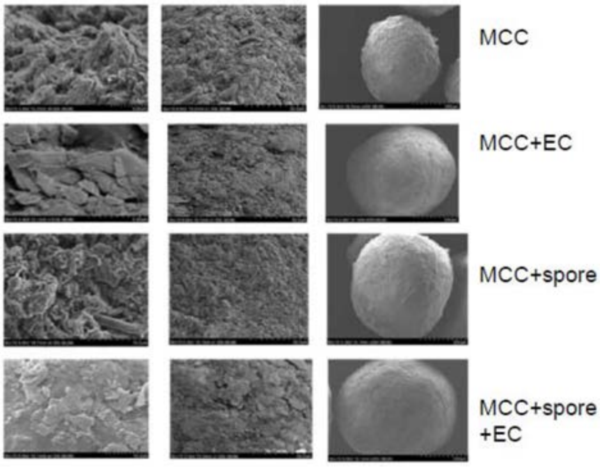

Fig. 14. An example of encapsulation process for a microbial system.

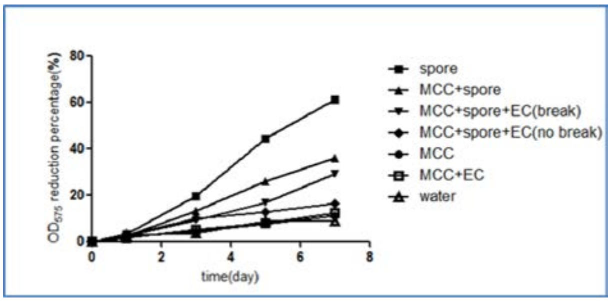

Fig. 15. An example of encapsulation process for a microbial system.

of a laboratory enrichment process from the Mangrove sediment [11]. Several important influence factors on bacterial precipitation of calcium have been further investigated, such as carbon source, nitrogen source, spore concentration, pH and so on).

The encapsulation process comprised: a) forming the grafted skeleton by using microcrystalline cellulose (MCC); b) mixing alkaliphilic spore with high mineralizing activity with MCC and c) encapsulating MCC + spore in ethyl cellulose (EC) or epoxy resin (ER) (see Fig. 14).

The survivability of the encapsulated bacteria was studied, together with the verification of protection functionality of microcapsule. It was found that the pure spore has the highest mineralizing activity. Broken microcapsules have higher mineralizing activity than non-broken ones, which indicate that EC microcapsules can effectively protect microorganism in this system (Fig. 15).

Evaluation of the resilience system

Two exciting moments will be demonstrated in this section concerning the evaluation of the resilience system. The first one is related to the microbial self-healing system. The encapsulated bacteria was cast in the cubic specimen (10 × 10 × 10 mm) made of cementitious

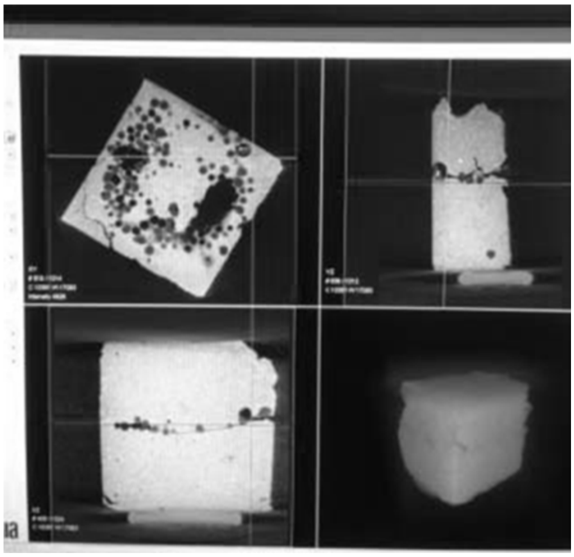

Fig. 16. Breaking of microcapsules and subsequent healing procedure (image of 3D X-ray Computed Tomography).

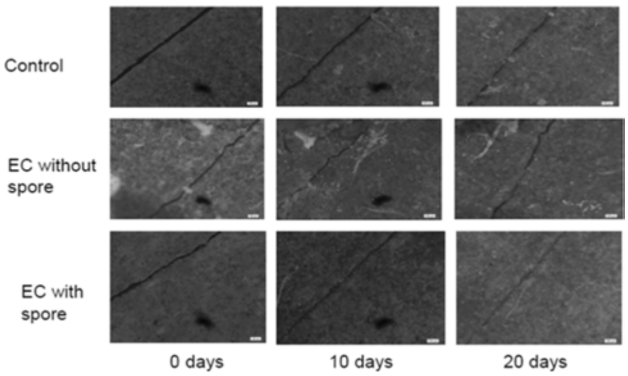

Fig. 17. Breaking of microcapsules and subsequent healing procedure (image of Environmental Scanning Electron Microscopy).

materials. After 14-day water-curing the specimen was subjected to a splitting procedure to create cracks in the cementitious material. The specimens were then placed in various curing conditions for a certain time. Fig. 16 shows a 3D XCT (X-ray Computed Tomography) image, where the calcium precipitation in the crack can be clearly identified. Fig. 17 shows another example of healing effect with the help of Environmental Scanning Electron Microscopy (crack width is ca. 20-50 micron.

The Ag-alginate based microcapsules were produced and mixed in cementitious matrix. After certain curing time, the specimen was put in the NaCl solution with different concentration (1 to 4 wt. %). After 7-day submerging, the situation was monitored by means of 3D X-ray CT. It is clearly seen that a lot of microcapsules disappear (see Fig. 18).

Challenges and Further Development

The evaluation of performance characterization of intelligent resilience system remains to be the tough

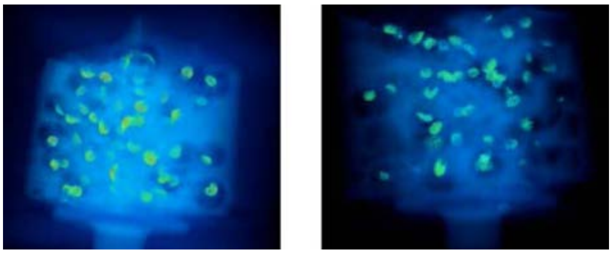

Fig. 18. Specimen without chloride penetration (left) and with chloride penetration (right).

challenge. Due to the inhomogeneity and randomness, bulk behavior of the cementitious system after resilience can hardly be experimentally evaluated at macro level. The only feasible way to do this is to go to the fundamental level to figure out the individual behavior of a single unit in the randomly distributed system. The relevant material properties are then determined experimentally with the help of specific facilitated test set-ups. Afterwards, numerical methods have to be exploited by means of obtained key parameters at micro level to simulate the bulk behavior of the resilient system.

To realize this the following working activities have to be fulfilled: a) working out a feasible and workable micro testing facilities; b) quantifying the relevant key parameters for various components (such as material properties of microcapsule, healing agent, interface between microcapsule and cement matrix, static and kinetic performance of healing process, etc.; c) quantifying the physical and chemical trigger mechanism and d) healing and recovery performance of single microcapsule system.

The behavior of single microcapsules in cement matrix was numerically studied at Shenzhen University [7]. The effect of physical trigger (cracking) on mechanical behaviors of the single microcapsule was simulated, whereas the size of microcapsule and the interface between the cement matrix and the microcapsule were considered as the key parameters (Fig. 19). Based on this valuable experience it was suggested that the some key parameters have to be experimentally determined in order to have a realistic picture.

Recently there have been two attempts at Shenzhen University towards this desired direction. Single microcapsule with different diameter and shell thickness were selected under optical stereoscopic microscope and then stick on the specimen stage. The micromechanical properties of single microcapsules such as Load-Displacement curve, modulus and rupture force were obtained by nanoindentor (see Fig. 20). The elastic modulus can be indirectly calculated. However, the strength of shell material itself needs to be further determined. The total mechanical behavior of single microcapsule should be simulated if the correct parameters are adopted.

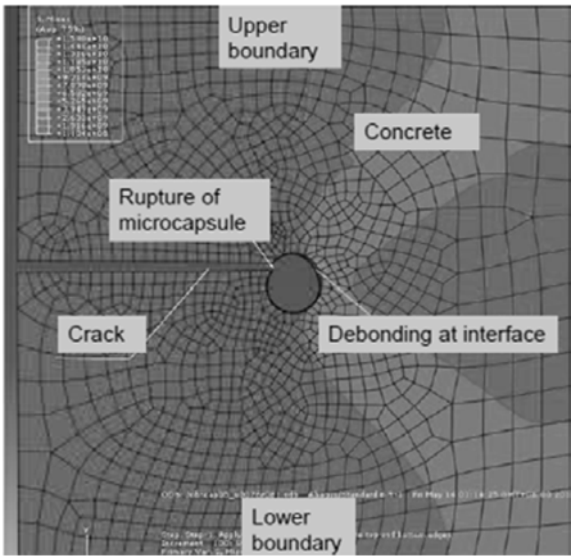

Fig. 19. Numerical simulation of a single microcapsule in cement matrix with a physical trigger.

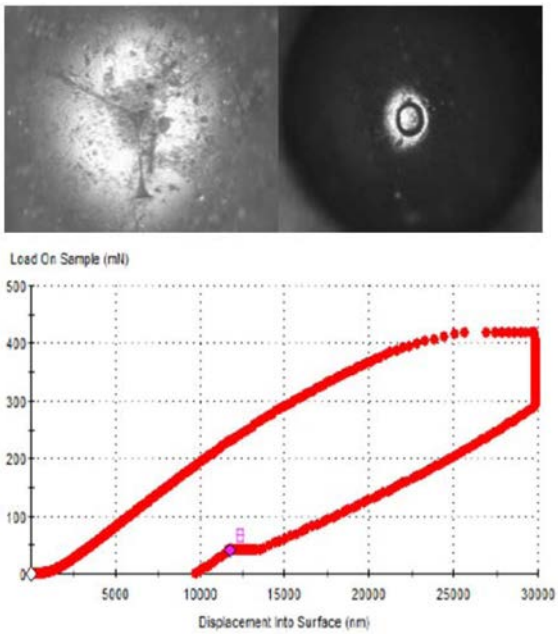

Fig. 20. Load-displacement curve of a single microcapsule obtained by nano-indentation test.

Another important parameter is the bond between the microcapsule and the cement matrix. A so called scarification test was carried out to determine the constitutive character of the adhesion (see Fig. 21).

The further development aims at creating intelligent resilience against attacks of the marine environment, resulting in infrastructures with durability properties that far exceed those of conventional ones. Multi-scale self-healing and self-recovery systems, embedded in the cementitious materials, will provide the required resilience. The main research attentions will focus on the following key issues, namely to:

(i) establish the relationship between the multi-

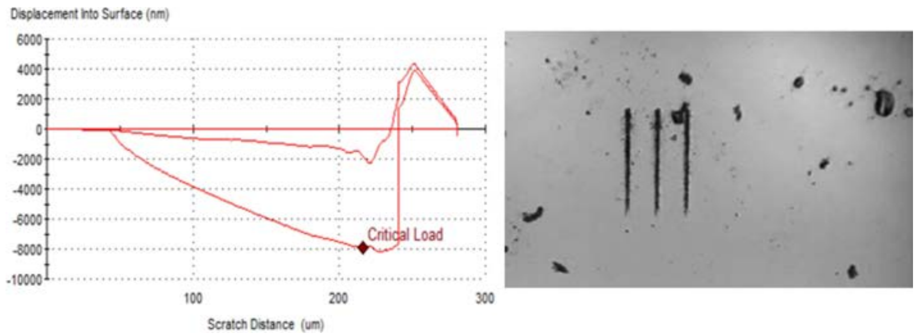

Fig. 21. Scarification test to determine the behavior between the microcapsule and the cement matrix.

actions and the action effect for cementitious materials;

(ii) link resilience requirements with the environmental action and the related degradation mechanisms;

(iii) incorporate existing self-healing and self-recovery systems to enhance the long-term performance of infrastructures by creating resilience to physical and chemical attack, through the addition of agents within microcapsules, that are able to mitigate the effects of a range of aggressive environments;

(iv) set up facilities and procedure to evaluate self-healing and self-recovery effect at micro level;

(v) quantify key parameters related to the fundamental material properties in order to supply the basic input for numerical simulations;

(vi) validate the design procedure and numerical model using data from bespoke tests at multi-scale;

(vii) demonstrate the intelligent resilience of the novel material system by using the experimental and numerical data.

Acknowledgments

The authors would like to acknowledge financial support provided by National Natural Science Foundation of China (No. 51120185002) and NSFC-Guangdong Joint funding (U1301241).

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