博士論文

Development of Cement Granules with Reserved Hydration Potential as Self-healing Additives

自己治癒用混和材として水和反応性を温存させたセメント造粒物の開発

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ABSTRACT

In the case of concrete structures, the long-time degradation process resulting from service loads and environmental exposure factors leads crack formation that gradually can cause a failure. Self-healing concrete is able to seal off crack routes through which deleterious substances are transported and prolong the service life of structures and minimizes the cost of rigorous maintenance. With the target of achieving sustainable infrastructures self-healing concrete, therefore, attracts a lot of research attention as a most promising study scheme.

Taking in to consideration the total advantages that could be obtained from such a material, several efforts have been invested in realization and application of self-healing concrete. The use of cementitious components to stimulate autogenous healing focusing on the addition of agents which are able to promote the deposition of crystals inside the crack is one main area of self-healing researches. Among these efforts include the use of powder type additives which are capable of expanding, swelling and precipitating up on contact with water. This method has later been upgraded to the granulation and semi encapsulation technique to overcome its drawbacks. There are still challenges involved with these two approaches and so are limiting factors. Incorporating powder type of additives highly affected the workability of the fresh mixes. On the other hand, having fully spreading efficient granules is expected to be improbable even if the granulation technique has minimal impact on fresh properties of concrete. Since during the agglomeration process water is used as a binding agent to manufacture the granules, initial hydration and hardening of the self-healing constituents becomes inevitable. Part of the hydration potential of the granules which could have contributed for the later crack closing process of the concrete is consumed during the granule manufacturing process itself.

In this study, in appreciation of the efforts of other researchers to realizing the improvement of self-healing concrete by incorporating cementitious components, two new approaches are suggested and investigated. It has been known that cementitious materials have natural autogenic healing capability due in part to the re-hydration of previously unhydratred cement remaining with in the matrix. It is with this background that compaction of cementitious powders and cement granulation using a mixture of non-reactive coating liquid and water were suggested to make self-healing additives having reserved cement hydration potential within them. This reserved reactivity

of the cement particles is later expected to come in to action and contribute to the self-healing process when crack occurs in the matured concrete matrix.

Previous studies conducted on recycling concrete by powder compaction by Sakai et. al. (2015) have revealed that it is possible to form solid compacts of cementitious materials by combining them with dry sludge powder. In this method, the use of water to make granules would not be required since the sludge powder could serve as a dry binding agent for the self- healing powders during compaction. In this study, powder compacted aggregates (PCA) made from sludge and ordinary Portland cement, blast furnace slag and fly ash were introduced as self-healing additives partially replacing sand. The PCA were prepared by compacting the powder mixtures inside a cylindrical mold using universal testing machine and crushing the resulting compacts by jaw crusher. After conducting water pass tests, it was shown that inclusion of the PCA contributes to water flow reduction. However, the performance of the samples incorporating PCA was not found out to be satisfactory given relatively young specimen of age 28 days were used for the experimental study. In addition, at the chosen formation pressures for the compacts the strength of the compacts themselves was very weak for the PCA to survive the mixing process of the mortar. Hence, the performance of the PCA could not be any advantageous over powder type self-healing additives (binary mixtures) with similar material compositions.

Meta (2018) indicated that the addition of coating liquid to mortar mixtures has a cement hydration reaction retarding effect there by resulting in disruption in mechanical strength development if used in large amount. This understanding has inspired the second series of trials to design cement granules with reserved hydration potential. This approach is considered to be advantageous over the former (PCA) approach as there would be no crushing for manufacturing the additives, hence, avoiding an expensive and an energy consuming process. Such types of cement granules are developed by making a balance between the ratio of total liquid to powder and the ratio of coating liquid to water. Two types of cementitious powders; ordinary Portland cement and silica fume, were agglomerated in mortar mixer with a mixture of the coating liquid and water to manufacture granules with reserved hydration potential. TG-DTA results confirmed that the inclusion of these granules in mortar samples show lesser degree of hydration compared to control samples which do not contain the granules. The addition of these cement granules resulted in water flow reduction reaching up to 85% for 28 days old samples and up to 70% for 91 days old samples of the test for an average crack width of 0.2 mm. For larger crack widths of 0.3 mm and greater, further research is suggested to improve the performance of granules or even consider other possible crack width limiting techniques.

Ikoma et al. (2014) has revealed that the initial high rate of flow reduction in water past test results is attributed to the generation of air bubbles with in the crack gap of concrete. Kayondo & Kishi (2016) pointed out that the formation of large air bubbles on crack surfaces will not occur when less than 100% air saturated water was used for water pass tests. Therefore, equilibrated water having an average DO content less than 95 % was utilized for conducting all water pass tests in this study to avoid the influence of large air bubbles on the water flow measurements. At the end of the 14th and 28th days of the water pass test, secondary vacuum soaking was introduced in this study following the same procedures as the initial one, to exclude effect of invisible air bubbles on the measured water flow and to verify the flow reduction resulting from solid precipitation and deposition only.

It is hoped that the progress and results of this study have highlighted the possible improvement of to crack healing ability by reserving initial hydration reactivity of cementitious additives. It is highly recommended that further research be conducted with several material combinations to achieve full crack closure and the extent of this possibility. In addition, long term healing capability of including granules prepared by using coating liquid needs to be studied.

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CHAPTER 1 INTRODUCTION

1.1 General

Cracks in concrete are a common phenomenon due to the relatively low tensile strength of concrete. Durability of concrete is impaired by these cracks since they provide an easy path for the transportation of liquids and gasses that potentially contain harmful substances. As a result of this periodic and routine maintenance are usually necessary to help sustain the performance of concrete structures.

Repairing and maintenance costs involved for concrete structures are usually high. Researches have pointed out that society is investing a huge amount of money for infrastructure maintenance [3]. It is also quite often that these repair procedures cannot be performed in some locations of defects due to inaccessibility. Therefore, it is important to control the crack width and to heal the cracks as soon as possible. Self-healing of cracks in concrete would contribute to a longer service life of concrete structures and would make the material not only more durable but also more sustainable.

With the target of achieving sustainable infrastructures self-healing concrete, therefore, attracts a lot of research attention as a most promising study scheme. Taking in to consideration the total advantages that could be obtained from such a material, several efforts have been invested in realization and application of self-healing concrete. The use of cementitious components to stimulate autogenous healing focusing on the addition of agents which are able to promote the deposition of crystals inside the crack is one main area of self-healing researches. Among these efforts include the use of powder type additives which are capable of expanding, swelling and precipitating up on contact with water and the use of semi encapsulated granules. Addition of such type of self-healing additives have shown promising results of crack closure compared to control samples without self-healing additives [4, 16, 19, 33, and 34].

On the other hand, there are still challenges involved with these two approaches and so are limiting factors. Incorporating powder type of additives highly affects the workability of fresh concrete mixes. On the other hand, having fully spreading efficient granules is expected to be improbable. Since during the agglomeration process water is used as a binding agent to manufacture the granules, initial hydration and hardening of the self-healing constituents becomes inevitable. Part of the hydration potential of the granules which could have contributed for the later crack closing process of the concrete is consumed during the granule manufacturing process itself.

In the midst of all these promising approaches to achieve efficient self-healing in concrete, two comparatively new techniques to include self-healing additives are suggested and being investigated in this research. It is well known that the powder compaction approach is a core manufacturing process in pharmaceutical, ceramics and metallurgy industries. This approach is currently under research to adopt it to recycling all components of concrete as a whole. This study exploits the possibility of utilizing powder compaction of cementitious powders with sludge powder obtained from concrete manufacturing plants to make self-healing additives which can partially substitute sand. This method is suggested to preserve self-healing additives from initial hardening by avoiding the use of water for binding cementitious powder particles; which otherwise is the main binder used for making granulated additives.

As a second alternative approach, cement granulation technique by using a coating liquid mixed with water is suggested to reserve the hydration potential of cement particles inside the agglomerates. Such types of cement granules with reserved hydration potential are developed by balancing ratios liquid mixture of water and coating liquid to powder materials and the ratio of coating liquid to water. The coating liquid added during the granulation process is expected to temporarily protect the granules from full hydration until crack happens and it gets washed away for their hydration to proceed and contribute to crack closing process.

1.2 Objective

The main purpose of this research is to propose a method to manufacture self-healing additives which have reserved cement hydration potential within them. It specifically attempts to

1. investigate the effect of including dry powder compacted additives on water flow reduction through cracks
2. examine the effect of sludge powder inclusion on self –healing ability
3. study the effect of inclusion of granules manufactured with a coating liquid on self-healing and estimate the amount of reserved hydration potential

In this study, in appreciation of the efforts of other researchers to realizing the improvement of self-healing concrete by incorporating cementitious components, two new approaches are investigated. It has been known that cementitious materials have natural autogenic healing capability due in part to the re-hydration of previously unhydratred cement remaining with in the matrix. It is with this background that compaction of cementitious powders and cement granulation using a mixture of non-reactive coating liquid and water were suggested to make self-healing additives having reserved cement hydration potential within them. This reserved reactivity of the additives is later expected to contribute to the self-healing ability when crack occurs in the matured concrete matrix.

The study aims to contribute to the efforts of a previous researches who were seeking to suggest ways to use cementitious materials as ingredients for self-healing concrete additives. It tries to shade light on ways to best save and utilize the remaining hydration potential in those cementitious materials and manufacture additives with minimal effect on the fresh and hardened properties of the resulting concrete. It is supposed that the results of this research will help to identify further research topics that can lead to full industrial application self-healing concrete technology.

1.3 Scope of the study

The experimental scope of this research is limited to laboratory experiments on mortar specimen to investigate the water flow reduction under static water condition. 28 and 91 days old specimen are chosen to consider the alteration in healing ability of the designed self-healing additives as the concrete starts aging. In addition, water to cement ratio of 0.5 is selected for the study specimen to minimize natural self-healing as much as possible and to better quantify the effect of inclosing designed self-healing additives.

The research is limited to investigating the self-healing ability self-healing additives designed to include only one type of coating liquid. Ordinary Portland cement and three pozzolanic materials; fly ash and blast furnace slag and silica fume, are selected as ingredients for manufacturing the additives. The use of other mineral and chemical admixtures and possible coating liquids is left as a suggestion for further investigation.

1.4 Outlines of the dissertation

Chapter one introduces the general background of this study and briefly presents the aim it targets to achieve along with the limitations.

Chapter two discusses about the current understanding and approaches to make a self-healing concrete. It identifies the differences between natural self-healing phenomenon in concrete and engineered self-healing by using additives capable of forming crack closing products. The development of cementitious materials as self-healing additives and the related advantages and limitations of different methods of manufacturing the additives are presented based on relevant literature reviews.

Chapter three gives a detailed description of the methods followed to manufacture powder compacted additives to partially replace sand in mortar samples. Powder compaction of ordinary Portland cement and supplementary cementitious materials together with sludge, which acts as a dry binding agent, is presented as an alternative way of manufacturing self-healing additives. The effect of inclusion of powder compacted self-healing additives on crack closing ability of mortar specimen is also presented in this chapter.

Chapter five investigates the self-healing ability of mortar incorporating granules manufactured with coating liquid. Cement granules with reservation hydration potential are manufactured by using a coating liquid and water mixture and granulating cement and/or silica fume powders in mortar mixer. This method of is suggested as a second alternative to powder compaction approach to reserve the hydration potential of cement and utilize it for self-healing contribution. The effect of using these self-healing additives as partial sand replacement on water flow reduction is discussed in this chapter.

Chapter six gives the general summary and conclusions drawn from the results of this research, furthermore, gives recommendations to the future studies.

CHAPTER 2 LITERATURE REVIEW

2.1 General

Concrete is one of the most widely used materials in the world, because of its strength, relatively lower cost and availability of its components. Concrete's versatility and global availability make it the world's first choice in many applications, above and below ground. It is also unique, being the only cold, moldable, inorganic plastic that can be used on a significant engineering scale. On the other hand concrete structures often suffer from cracking and related much earlier deterioration from the designated design service life.

Generally speaking cracks in concrete can occur in any stage of the service life of concrete. The cause of concrete cracks may be classified as primary and secondary causes. Cracks formed by primary causes are considered as structural damage and are more serious ones. Primary cracks occur due to overloading, insufficient amount of reinforcing steel, deflections, poor detailing and others. Secondary causes are more of inherent properties of concrete due to volume instabilities such as autogenous shrinkage and/or drying shrinkage, plastic shrinkage and temperature effects since concrete is composed of aggregate of various sizes connected with the hydration products generated by mixing cement and water [1].

Durability of concrete is impaired by these cracks since they provide an easy path for the transportation of liquids and gasses that potentially contain harmful substances. If micro-cracks grow and reach the reinforcement, not only the stiffness is reduced, but also the reinforcement will be corroded. The appearance of these micro-cracks in concrete is unavoidable, not necessarily causing a risk of collapse for the structure, but certainly accelerating its degradation and diminishing the service life and sustainability of constructions.

Van Bruegel (2007) presented a graph which described the performance of structures with elapse of time (see Fig. 2.1). Gradual degradation occurs in normal quality infrastructures until the moment that first repair is urgently needed. Yet there is still a point of concern which is the durability of infrastructures after repairs. Very often a second repair is necessary only ten to fifteen years later. Spending more money initially in order to ensure a higher quality infrastructure often pays off. The maintenance-free period will be longer and the first major repair work can often be postponed for many years. [2].

Nonetheless, repairing and maintenance costs involved for concrete structures are usually high. Now a days, different researches indicate that society is investing huge amount of money due to low quality and durability issues of concrete. For instance, 50 % of Europe's annual budget is spent on rehabilitation and maintenance of concrete infrastructures. In United States, 5.2 billion US dollar is spent on average for only bridge repair and maintenance [3].

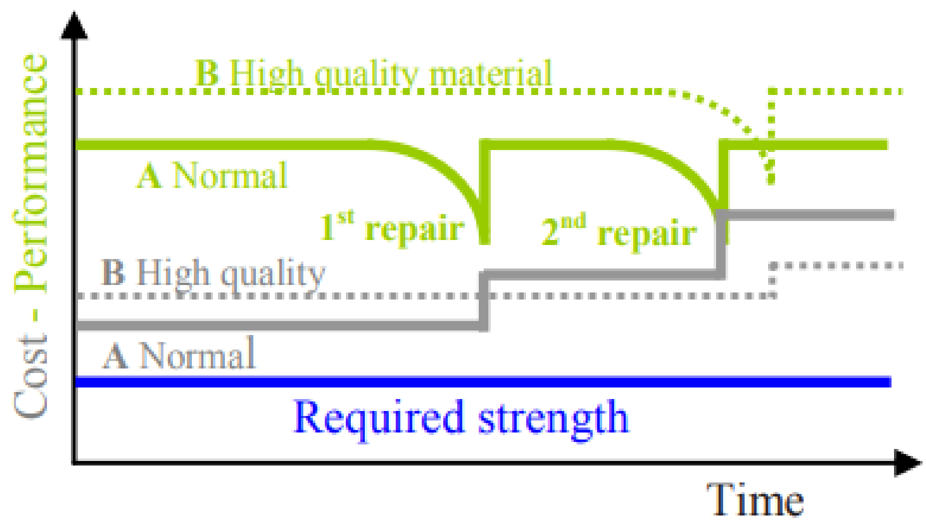


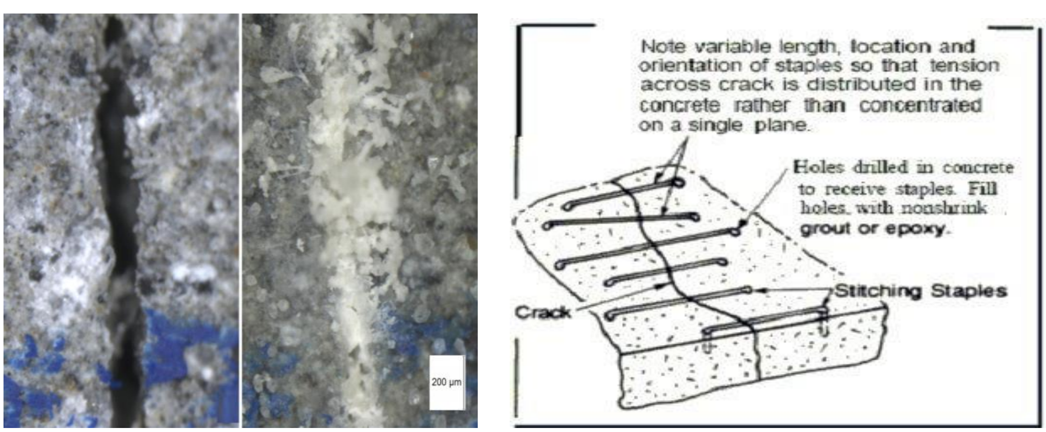
Figure 2.1 Performance and cost, including direct repair cost vs. elapse time for (A) normal and (B) high quality infrastructure [2]

Additionally, in some cases, it is difficult for engineers to access the damaged sites for repair work because of their locations and/or environmental conditions. Some examples are underground structural members, radioactive waste disposal facilities, and walls of tanks storing highly toxic waste [1]. It was these problems of high infrastructure repair costs and accessibility difficulties which led Civil Engineers to look for a suitable and sustainable solution rather than the traditional repair approaches.

To prevent deterioration, regular inspection of cracks in concrete structures and their repairs are carried out by means of some kind of human intervention. On the other hand, in nature, animals and plants are capable of healing small bodily damage by themselves. The term self-healing brings to mind something biological and indeed, self-repair is a hallmark of living things from microscopic level repair of cell wall to macroscopic level of wound and broken bone repair. Nature, therefore, has been the source of inspiration for coming up with the idea of self-healing materials [1, 6].

In 1994, C. Dry was the first who proposed the intentional introduction of self-healing properties of concrete. In the following years several researchers started to investigate this topic. Among these several approaches some aimed at improving the natural autogenous crack healing while others aimed at modifying concrete by embedding capsules with suitable healing agents [7]. Many techniques and methods have been developed according to the different intrinsic properties of the various material classes. However, the common feature is all of these self-healing materials are able to sense 'damage' and self-repair, thus, demonstrate 'continuous renewal' of their performance [3].

Existence or availability of self-healing and self-repairing systems would make infrastructures more reliable. For instance, at early stage, if it were possible to control and repair cracks, permeation of driving factors for deterioration could be prevented which will play a great role on extending the service life of structures[5]. According to Ahn & Kishi (2010), the serviceability limit of concrete structures by cracking might be overcome by crack control methodologies; the enhanced service life of concrete structures would reduce the demand for crack maintenance and repair. In particular, the utilization of self-healing technologies has high potential as a new repair method for cracked concrete under the water leakage of underground civil infrastructure [4]. Figure 2.2 shows the comparison between self-healing of cracks and traditional crack repairing system [5].



a. Self -healing of concrete b. Concrete crack repair by stitching

Figure 2.2 Self-healing of concrete vs. traditional crack repairing method [5]

Van Breugel (2007) argued “Enhancing the longevity of our built infrastructure will surely reduce the impact of mankind’s activities on the stability of the biosphere”. For instance, enhanced infrastructure service life will lessen the demand of new infrastructures resulting low raw material usage. On its turn, it reduces energy consumption and decrease related CO_2 emission [2, 3].on the other hand, self-healing concrete is expected to have a higher initial cost than traditional concrete. However, in the long run, there will be savings in maintenance costs perhaps of the order of 30% as contended by Ahn and kishi (2010) [4]. For infrastructures the ideal case would be that no costs for maintenance and repair have to be considered at all because the material is able to repair itself as depicted in Fig. 2 by Van Breugel (2007).

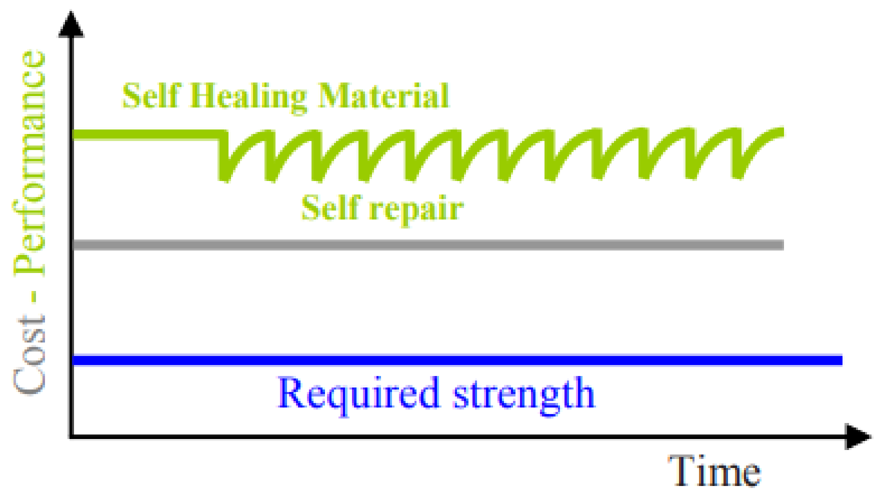


Figure 2.3 Performance and cost vs. elapsed time for structure built with self-healing material [2]

2.1.1 Definition of important terms

The Technical Committee on Autogenous Healing in Cementitious Materials (Technical Committee Reports 2009) in Japan Concrete Institute with the aim of quantification of self-healing on various scales, conducted literature surveys and discussions in 2009.

Table 2.1 Mechanisms and classification of phenomena [8]

Natural healing: is defined as a phenomenon in which cracks in concrete are naturally clogged in an environment involving moisture, for instance, without any special arrangement in the material design etc.
Autonomic healing: A phenomenon in which cracks are clogged in concrete made with special material design, such as the use of an appropriate supplementary cementing material in expectation of its effect of clogging or accelerating the clogging of cracks in the concrete in an environment involving moisture etc.
Activated repairing: A phenomenon in which cracks are clogged in concrete by a mechanism of devices embedded in the concrete beforehand for the purpose of autonomic ally repairing cracks.
Autogenous healing: A concept encompassing natural healing and autonomic healing; the whole phenomenon of cracks in concrete being clogged by in an environment involving moisture, etc.
Engineered healing/repairing: A concept encompassing autonomic healing and activated repairing; a phenomenon in which cracks in concrete are clogged by the use of the concrete made with special material design to clog/repair cracks.
Self-healing/repairing: The whole phenomenon of clogging of cracks in concrete not by human hand.

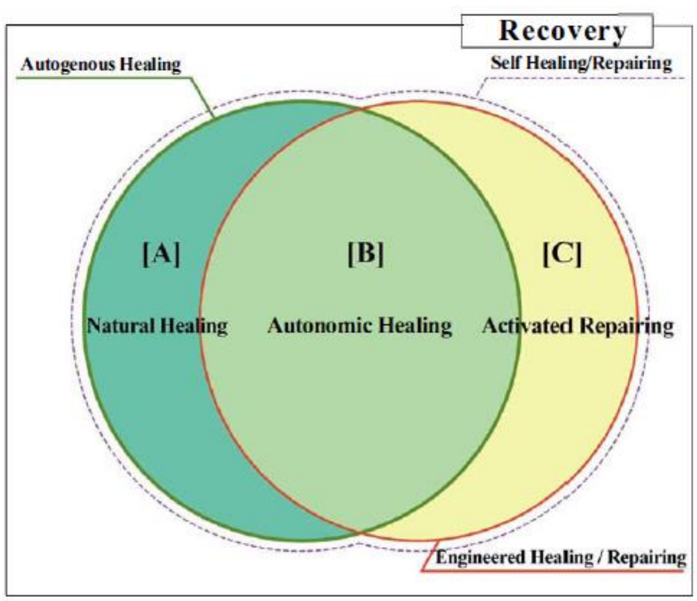


Figure 2.4 Classification and Venn diagram of self-healing/ repairing of crack [8]

2.2 Natural self-healing in concrete

The phenomenon of self-healing in concrete has been known for many years. It is understood that concrete generally possess an innate self-healing character due to its material components. When water comes in contact with the un-hydrated cement, further hydration occurs. Furthermore, dissolved CO_2 reacts with Ca^{2+} to form $CaCO_3$ crystals. These two mechanisms, however, may only heal small cracks [9]. Besides, this natural self-healing capacity is only effective when water is available and is difficult to control. As shown in Fig. 2.5, in natural self-healing processes, four following progressions can block cracks in concrete [12];

(A) The formation of calcium carbonate or calcium hydroxide is another process to block crack,

(B) Crack blockage by impurities in the presence of water,

(C) Further blockage of crack by hydration of the unreacted cement or cementitious material,

(D) Crack can blocked by the expansion of hydrated cementitious matrix in the crack gaps (swelling of calcium silicate hydrate gel)

In many cases, more than one of these process or mechanisms (Fig. 2.5A to 2.5D) can happen simultaneously. Among the proposed self-healing mechanisms in the natural process, formation of calcium carbonate and calcium hydroxide (Figure 2.5 A) are the most effective methods to heal concrete naturally [10]. This view is supported by the fact that some white residue can be found on the outer surface of the concrete cracks. This white residue is found to be calcium carbonate and has been widely reported. [10, 13].

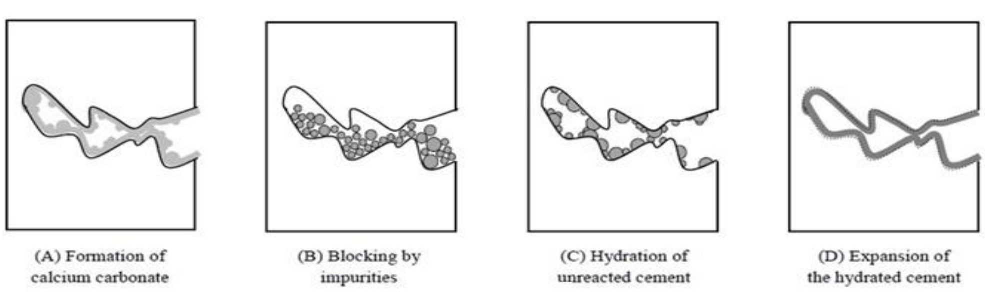


Figure 2.5 Possible mechanisms for natural self-healing in cementations material [10, 11]

The fundamental mechanisms for the formation of calcium carbonate and calcium hydroxide are represented in Eqn. (2.1) to (2.3). At the first step, carbon dioxide is dissolved in water.

$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$ ……………………..Eqn. (2.1)

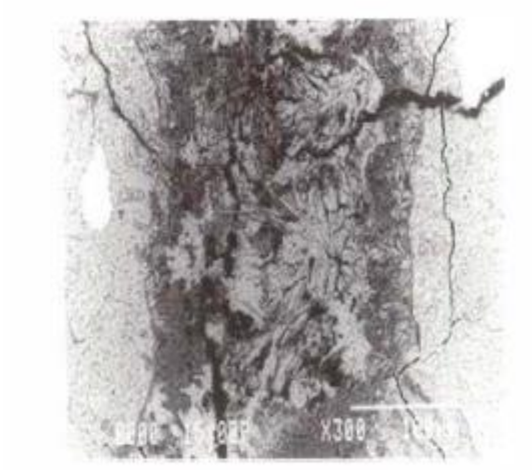
Free calcium ions are released as a result of cement hydration and dissipation through concrete as well as long the cracking surfaces reacts with CO_3^{2-} and HCO_3^-. As a result, calcium carbonate crystals are formed. Reaction (2) and (3) can only happen at pH values above 7.5. The crystals grow both at the surface of the cracks and finally fill the gap.

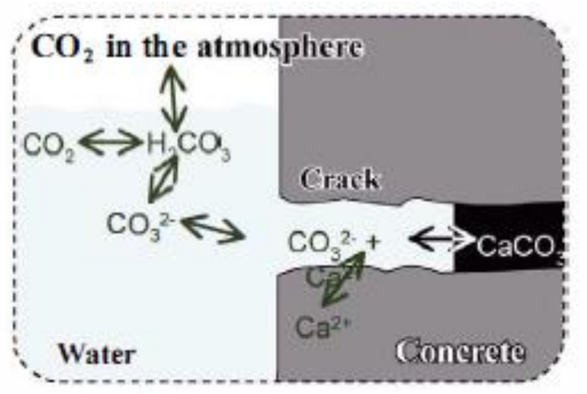
$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$ ………………………………………………………………..Eqn. (2.2)

$Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3 + H^+$………………………………………….…………………..Eqn. (2.1)

Neville (2002) claimed that, further hydration of anhydrate cementations components is mainly due to the natural self-healing properties in concrete. However, this process only applies to very young concrete and the formation of calcium carbonate most likely causes self-healing at later ages [14]. Natural self-healing can be useful for cracks with widths up to 0.1–0.2 mm [15]. In fact, most of these mechanisms can only partially fill the entrance of some cracks and cannot completely fill the cracks. This will be useful to prevent the development of cracks or prevention of deep penetration of harmful chemicals such as acids into the crack.

The presence of natural self-healing ability of concrete is exemplified by the JCI Technical committee reports. It was shown that the cause of crack closure may not be restricted to the precipitation of calcite but also formation of other hydration products such as etterngite and MgO could contribute to natural self-healing process. It has also been shown that other products such as ettringite and magnesium hydroxide could be useful to closure cracks in concrete. Fig. 2.6 shows an example of natura1 hea1ing in concrete. It shows a concrete specimen having artificia1 cracking induced and then exposed to a tida1 zone environment for 15 years. Most cracks with a sma11 width (around 0.5 mm or less) have been natura11y hea1ed. The substances c1ogging the cracks are reported to be primarily ettringite with needle-like crysta1s and magnesium hydroxide [8].





(a) (b)

Figure 2.6 Example of natural healing in hydraulic structures (a) Ettringite and Magnesium hydroxide depositing near cracking (b) Mechanism of natural healing [8]

2.2.1 Factors that could promote the natural self-healing process in concrete

I. Low water to cement ratio and young age of concrete

At the early stages of concrete, there is a lot amount of un-reacted cement particles. Therefore, the continuing of hydration of un-reacted cements when crack penetration and contacting with water is believed as the main mechanism for crack filling. With the elapse of time, it is thought that almost all cement in concrete is hydrated and the crack healing in old or mature concrete will occur mainly due to the dissolution or precipitation of calcium carbonates. However, this scenario preferably takes place in concrete using huge amount of cement or low W/C ratio, and the crack width should not be too large, typically less than 0.1 mm. Moreover, it is difficult to control or determine the healing capacity in these cases [16].

The water ratio between 0.40 and 0.55 is usually used in practical concrete mixtures. A recent research shows that at W/C of 0.40, about 20-30% of un-hydrated cement is left in the concrete which is important for autogenous self-healing of cracks in concrete [16]. This is the reason why concrete naturally possesses self- healing capacity due to continued cement hydration. When cracks occur and become vulnerable to water, un-hydrated cement will be reacted to water to form healing products at the crack that may penetrate the cement matrix.

For example, Fig. 2.7 shows an increase in healing with higher water-cement ratios, in which 1-90 day means the initial breaking age was 1 day and then curing was done for 90 days until the testing of the healing effect. On the basis of the results of microscopic examination, it was concluded that the bonding materials formed during the action were 100% calcium carbonate $CaCO_3$ and calcium hydroxide $Ca(OH)_2$ crystals but that no amorphous hydrated products of cement were found, though the test samples were young (1 to 28 days) [8].

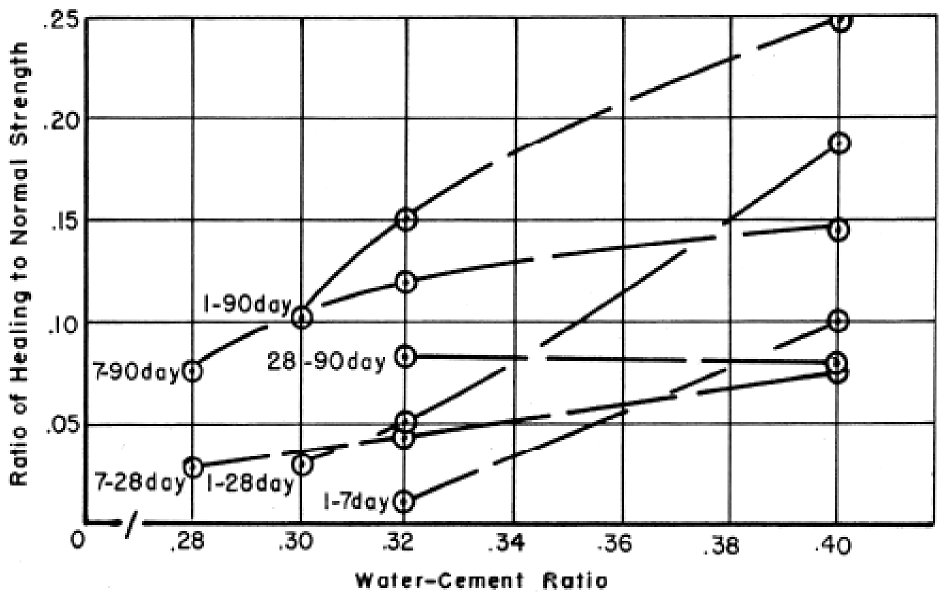


Figure 2.7 Plot of ratio of healing to normal strength versus water cement (Lauer and slate, 1956) [8]

Dhir et al. (1973) studied the influence of age and mix proportions on self-healing mortars. It was concluded that the rate of healing decreased with age within the test range of 7-120 days. The percentage of strength recovery was greater for mixes with higher cement contents. They also concluded that the ultimate strain of healed specimen was reduced [8].

Hearn and Marley (1997) carried out a permeability test (see Fig. 2.8) with 26 years old concrete and confirmed that drying and re-saturation resulted in a substantial increase in the self-healing effect and that extensive micro-cracking due to drying stimulated the effect since most of the flow took place through cracks exposed to the atmosphere [17].

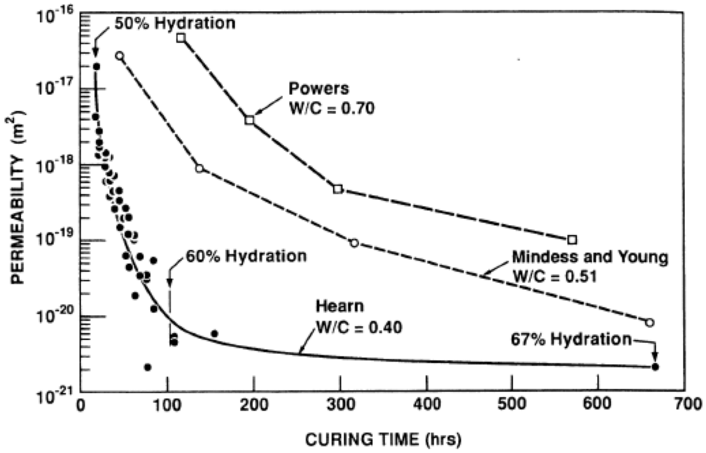


Figure 2.8 Permeability vs. Extent of hydration [17]

II. Larger grain size of cement particles

Cementitious materials have been observed for many years to have natural autogenic healing capability due in part to the re-hydration of previously unhydratred cement remaining with in the matrix [4]. Sawaki & Sakai (2007) indicated that old hardened cements dating back to the Meiji era still contained unhydrated cement particles of several hundred μm or larger. On the other hand, the fineness of Portland cement has been improved due to advancements in clinker crushing technologies and hardened cement made in more recent ages contained unhydrated cement particles smaller than 100 μm in diameter [18]. Even if very old hardened cements contain big sized unhydrated cement particles, those particles are not expected to contribute to the natural self-healing potential because they will be very strong to be breakable at cracking [19].

2.3 Engineered self-healing in concrete using cementitious materials

Engineered self-healing encompasses autonomic healing and activated repairing; a phenomenon in which cracks in concrete are clogged by the use of the concrete made with special material design to clog/repair cracks (see Fig. 2.4 and Table 2.1). Concrete is designed to be self-healing with special material design, such as the use of an appropriate supplementary cementing material in expectation of its effect of clogging or accelerating the clogging of cracks or by a mechanism of devices embedded in the concrete beforehand for the purpose of autonomic ally repairing cracks.

There are variety of approaches to engineered self-healing concrete design. However, most of them are under development stage in the laboratory. Muhammad et al. (2016) summarizes cement based self-healing researches as shown in Fig. 2.9. The presented taxonomy of cement based self-healing research classified the development of self-healing in cement based materials to be obtained as natural phenomenon or artificial phenomenon. The term 'Artificial healing' is adopted in the study to address the type of healing other than the natural innate capability to close cracks. This is in good agreement with the classification taxonomy given by the JCI technical committee as an 'engineered self-healing" [8, 20]. In the later, filling of cracks is triggered by addition of supplementary cementing materials to the concrete mix or steel fibers. Polymers and microorganisms were also used to mimic nature (see Fig 2.9). The width of the cracked healed by these approaches was assessed using microscope and it is presented in Table 2.2.

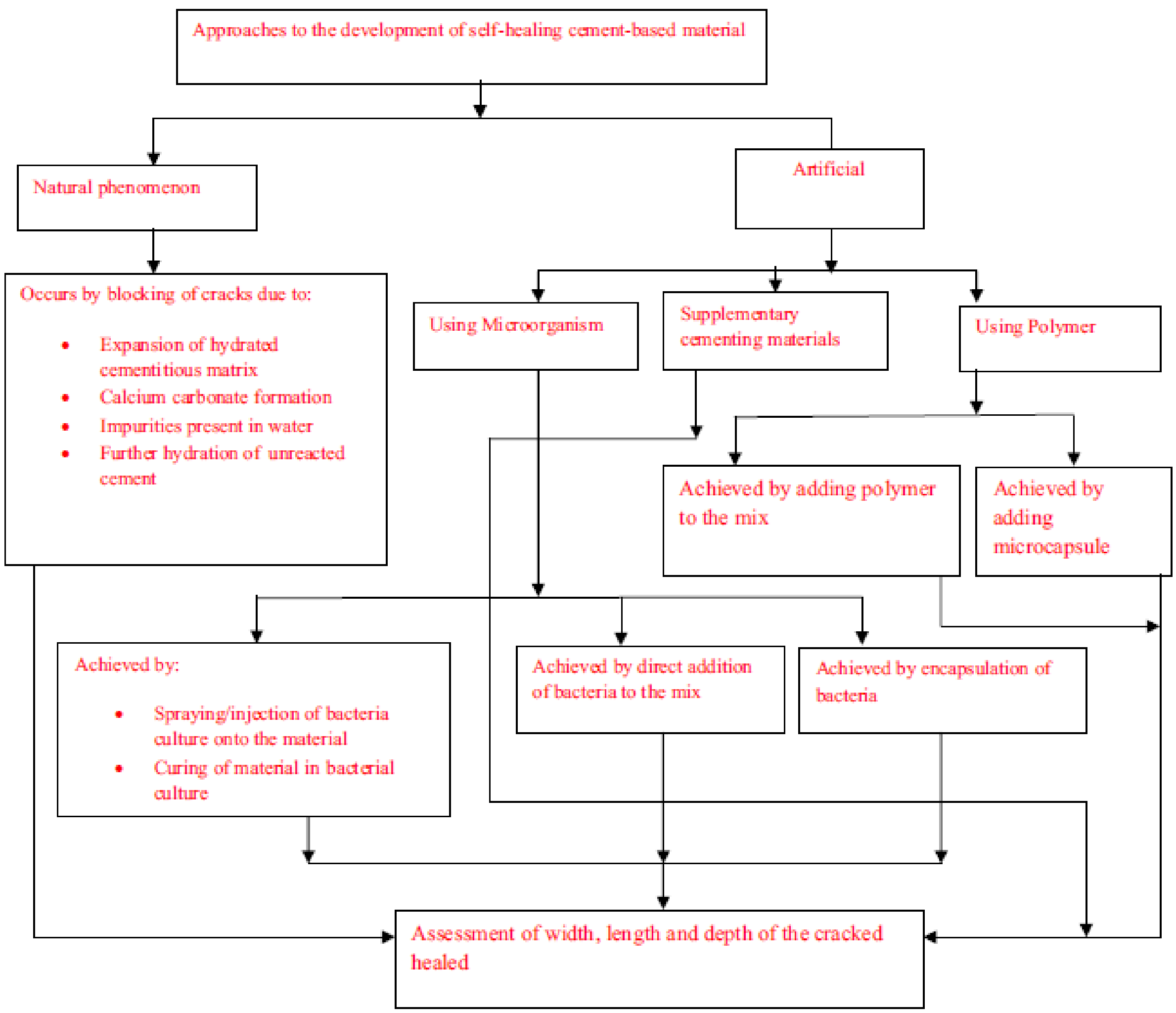


Figure 2.9 Taxonomy of cement based self-healing research [20]

Regarding the microorganism approach, Tittelboom et. al. (2013) summarized that self-healing by bacteria embedded in hard-shelled algae (DE), microcapsules or super absorbent polymers (SAP) is quite close to practical applications these agents can survive the concrete mixing process and can thus easily be added upon concrete manufacturing. However, some work will have to be dedicated to the reduction of the cost of the bacteria and thus to allow upscaling of the bacteria production. In addition, work is needed to make sure that the decrease in strength due to the presence of the nutrients and carriers, remains limited [7, 21].

Addition of polymers or micro capsules to concrete is also another frontier of the self-healing researches. Studies on the autogenous healing behavior inside polymer modified concrete which is made by the dispersion of organic polymers inside the mixing water of concrete. Upon cement hydration, coalescence of the polymers occurs resulting in a co-matrix of hydrated cement and polymer film throughout the concrete. Abd-Emoaty (2011) stated that healing in polymer modified concrete occurred in the same way as in traditional concrete. However, healing occurred to a larger extent and was extended over a longer period compared to traditional concrete as more unhydratred cement was available in the matrix because the polymers enclosed the cement particles as a kind of membrane Capsule based self-healing materials sequester a healing agent inside discrete capsules. When the capsules are ruptured, for example by damage, the self-healing mechanism is triggered through the release and reaction of the healing agent in the region of damage [7, 22]. However, one main challenge for practical applicability of these techniques would be the high cost of the polymers and the micro capsules.

Table 2.2 Self-healing approach and measured variables [20]

Approach	**Measured Variable (Width of the crack)**
Natural	Healing of crack below 60 µm was reported
Supplementary cementing material	Crack width below 200 µm could be plugged
Polymer	Crack width up to 138 µm was completely filled
Bacteria and Encapsulation/ Immobilization	Healing of maximum crack width of 0.970 mm was reported
Other (Biological and chemical)	Healing of Crack width up to 0.22 mm was reported

The third approach of artificial (engineered) self-healing concrete researches as presented by Muhammed et al. (2016) is the use of supplementary cementing materials (see Fig. 2.9). The term supplementary cementing materials is related to addition of materials that contribute to the properties of hardened concrete through hydraulic or pozzolanic activity. Typical examples are fly ash, slag cement (ground, granulated blast-furnace slag), and silica fume [23]. Moreover, there still are other attempts to stimulate autogenous healing, and design self-healing concrete focusing on the addition of agents which are able to promote the precipitation and deposition of crystals inside the crack.

The development of engineered self-healing concrete with supplementary cementitious materials and mineral admixtures with various crack closing capabilities is the main interest of this dissertation. These materials are considered as advantageous to use for self-healing material inputs because they have good compatibility with the cement matrix and lower costs when compared to inclusion of microorganisms or polymers. According to Tittelboom et al. (2013), a disadvantage of applying particles which may further hydrate or crystallize is that their healing functionality is limited as the healing agent itself is consumed in the process [7]. This presents a challenge on their practical applicability for engineering infrastructures.

2.3.1 Mineral admixtures (powder) approach

I. Supplementary cementitious materials/pozzolanic powders

The replacement of cement with supplementary cementitious materials has been known to improve the mechanical properties of concrete and its durability. In addition, some of these materials are considered as waste by products of other production industries hence their use in concrete production (or as partial cement replacement) is considered to play role in ensuring environmental preservation by reducing the use of cement which is produced by high energy consuming process.

A Pozzolan is defined as “siliceous or siliceous and aluminous materials which in in itself possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. This chemical reaction between a Pozzolan, calcium hydroxide and water which yields C-S-H gel is called the pozzolanic reaction [24, 25]. In self-healing concrete made with supplementary cementitious materials, this pozzolanic reaction forms a new product similar to hydration products in cement is formed filling the crack gap.

Baert (2009), stated that the low reactivity of these materials and the possible presence of those materials remaining unreacted over long period of time contributes to the self-healing capability of concrete incorporating pozzolanic materials [26]. Pipat et al. (2009) measured the hydration degree of the cement and fly ash as functions of time where the hydration degree is defined as the amount of the hydrated part divided by the total amount before the hydration reaction. Comparing between the cement paste and the fly ash–cement paste, the hydration degree of cement in the cement paste was slightly lower than those in the fly ash–cement paste. Nevertheless, the difference could be neglected at higher ages. In contrast, the hydration degree of fly ash was very low before 28 days. However, from 28 days to 91 days, the hydration degree of fly ash increased rapidly and was still gradually increasing at later ages (see Fig. 2.10). Fig. 2.10 shows the amounts of hydrated cement and fly ash as functions of time. In Fig 2.10 the hydration degree of fly ash in FA 15% was higher than those in FA 25% and FA 50%. In Fig. 2.11, however, the amount of hydrated fly ash in FA 50% was higher than those in FA 25% and FA 15%. The total hydrated particles (cement and fly ash) decreased when the replacement ratio of fly ash increased [24].

Several researchers [24, 26-28] have reported the incorporation of supplementary materials particularly fly ash and blast furnace slag in concrete not only brings about the improvement of mechanical properties but also results in better self-healing capabilities when compared to control samples without these supplementary cementitious materials. It is worth to note that there might be a tendency for the need of high replacement ratio of pozzolanic materials to lower the initial degree of hydration and to make effective self-healing concrete for practical applications. Haoliang et al. (2014) demonstrated that cement paste containing high percentage of slag (66% in the study) can be more efficient than in a Portland cement paste [28]. Pipat et al. (2009) stated that in long term case, $Ca(OH)_2$ may not exist anymore due to carbonation [24]. This fact brings a challenge and the need for more studies to practically apply concrete for applications.

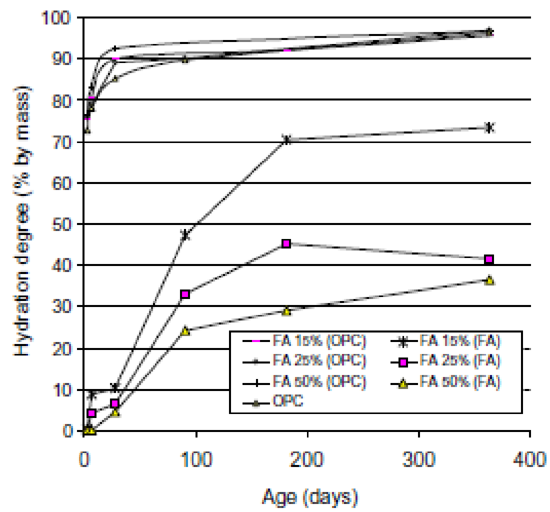


Figure 2.10 The hydration degree of cement and fly ash as a function of time [24]

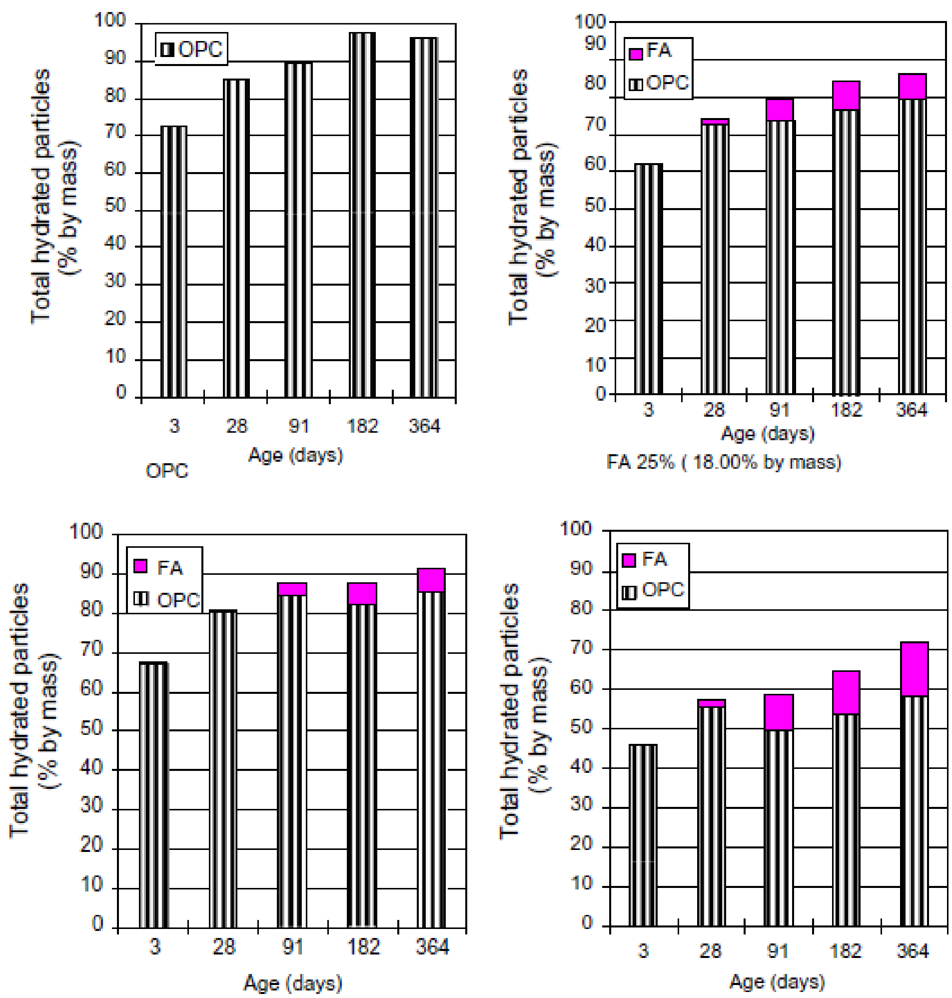


Figure 2.11 The amount of hydrated cement and fly ash as a function of time [24]

II. Engineered self-healing with mineral admixtures

Self-healing can be attributed to reactions of mineral admixtures in cementitious materials. These mineral admixtures are added in the concrete mixture during mixing. After concrete cracks, some un-reacted mineral admixtures are present at crack surfaces. When water penetrates into the cracks, these mineral admixtures start to react with water in the cracks. The cracks are then expected to be filled with reaction products. The mineral additives utilized for self-healing can be categorized into two groups: expansive additive and crystalline additive.

Expansive agents are added to concrete primarily for shrinkage compensation to prevent early cracking. Kishi et al. (2007) investigated the self-healing properties of concrete incorporating expansive agent as partial cement replacement in terms of recrystallization on cracked concrete as well as the effects of various carbonates for the recrystallization. It was shown that cementitious crystallization was induced resulting in the precipitation of calcium salts in the cracks because of the general increase in the OH^- and $SO4^{2-}$ concentration in the pore solution. Expansive agent also seemed to play a role in the formation of various AFm phases and Hemicarboaluminate for the crystalline phases. Fig.2.12 presents the effects of various carbonates and expansion agent in concrete [30].

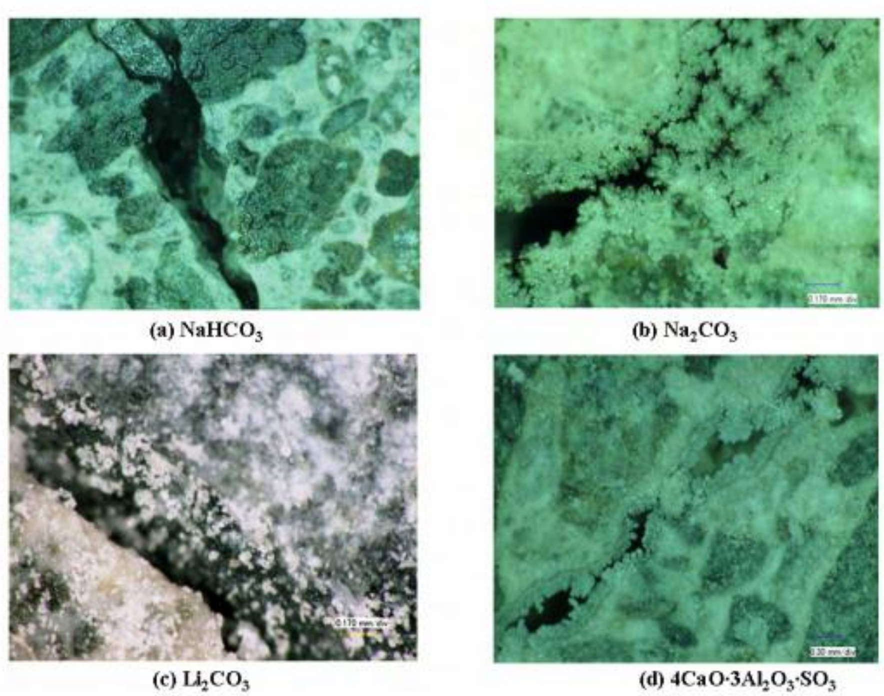


Figure 2.12 Effects of various carbonates and C_4A_3S on the self-healing of cracks [30]

Similarly, K. Sisomphon et al. has reported the self-healing potential of cement based materials incorporating capsized tri calcium sulfoaluminate based expansive additive (CSA) and crystalline additive (CA). After the mortar specimen were submerged in water to create self-healing process, the mixtures with CSA and CA showed favorable crack closing ability. It was hypothesized that the amount of leached Ca^{2+} from the matrix plays an important role on the precipitation of calcium carbonate which is the major healing product [31].

III. Engineered self-healing with expansive, swelling and precipitating terms

Ahn (2007) developed a combination of powder type self-healing additives which consisted of K K type of expansive agent, two types of geo materials and chemical agents. The K type expansive agent consisted of three mineral admixtures C_4A_3S (Hauyne), $CaS0_4$ (ahhydrite) and CaO (free lime). The geo materials mainly consisted of SiO_2, Al_2O_3 and were capable of swelling 15-18 times of their dry size when wetted by water since they contain swelling clay material. In the case of the chemical agents, various types of carbonates were selected to incorporate cementitious recrystallization to fill crack gaps. For concrete containing these composite cementitious admixtures, it was reported that crack-width of 0.15 mm could be healed after re-curing for 3 days while the crack width decreased from 0.22 mm to 0.16 mm after re-curing for 7 days. Complete healing of the cracks could be achieved after 33 days of re-curing [4,33].

It was observed that the self-healing phenomenon occurred mainly because of the swelling effect of the geo materials, expansion effect from the expansive agent and re-crystallization of the chemical admixtures contained in the powder types of additives (see Fig 2.13). From the study, it is considered that the utilization of appropriate dosages of geo-materials and expansive agents has a high potential as a new repairing methods of cracked concrete under the water leakage of underground civil infrastructures such as tunnels. However, since the powder type of additives have high surface area, the workability of the mix was severely affected (see Fig 2.14). At water to cement ratio 0.45 even after the addition of 2% superplasticizer some of the concrete mixtures were showing a slump loss up to 25 mm compared to the target flow (105 mm).

Using these type of mineral admixtures as self-healing agent have some advantages. For example some minerals are able to react intensively with water, self-healing of cracks proceeds fast. Moreover, because of their expansive character, the expansive additive can definitely improve the efficiency of self-healing.

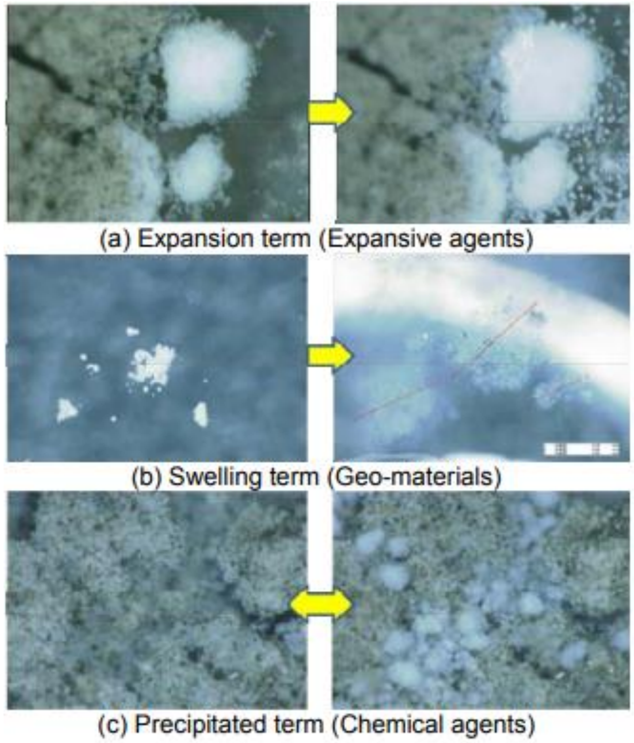


Figure 2.13 Design of cementitious composite materials with self-healing capability [4, 33]

Amid its advantage, there are some technical problems when mineral admixtures are used as self-healing agent. For instance, if the minerals are directly added into the concrete mixtures without any protection, once they come in contact with water during the mixing of concrete, they immediately start to react. As a result, these added minerals are consumed before cracking. Moreover, when an expansive additive is used, expansion always occurs in the interior of the concrete matrix, which could cause damage. Also the inclusion of self-healing powder into concrete mixture caused a significant reduction in the workability of fresh concrete and possibly reduced the self-healing efficiency of hardened concrete, due to unavoidable further reactions between the embedded powder, water and other products during the mixing and hardening process of concrete [32].

One more important requirement for this self-healing mechanism is that water should be continuously available in cracks, the same as autogenous self-healing. Similar to the case of autogenous self-healing, ions coming from environment have significant effect on physicochemical processes of self-healing based on mineral admixtures. However, by now there are no studies reported about the effect of ions from environment on self-healing in cementitious materials based on mineral admixtures. Some ingressive ions may promote self-healing, while some may inhibit. It is suggested that the effect of ingressive ions on the healing process should be taken into account in future research [7].

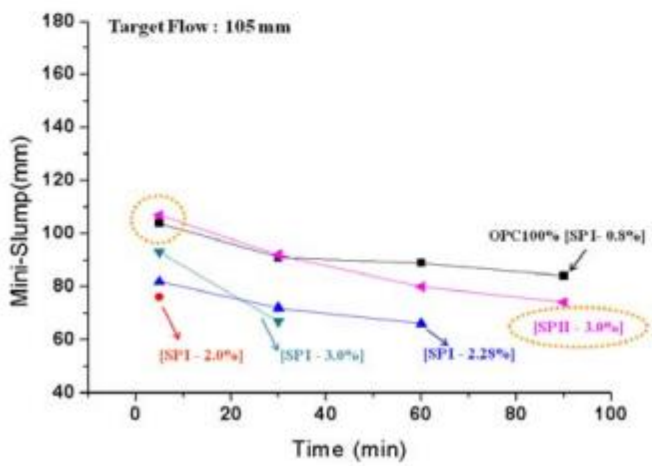


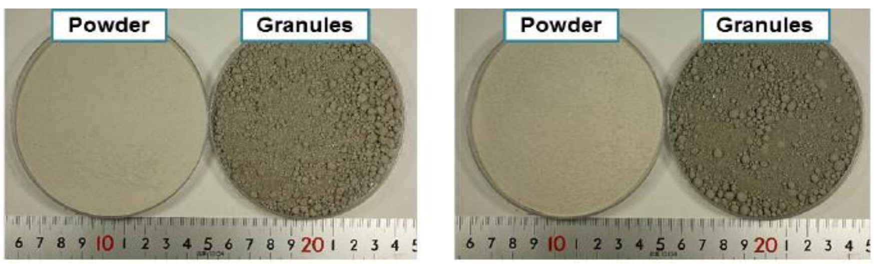
Figure 2.14 Effect of the addition of superplasticizers on the mini-slump of cementitious composite pastes in case of Sample I (OPC 90% + CSA 5% + Geo-materials 5%; three-component system, Water/Binder ratio = 0.45) [4, 33]

2.3.2 Granulation and semi-capsulation approach

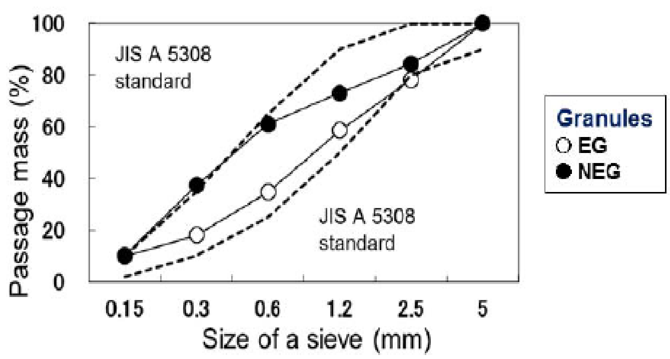
Granulation and semi encapsulation of cementitious powders and mineral admixtures for partially replacing the sand was proposed by Koide and Morita (2010) to overcome the challenges of using powder type self-healing additives. Powder type of self-healing additives were reported to highly affect the workability of the mix and since they are added to the mix without any protection they immediately begin to react bringing the long term healing capability in to question [16].

In the granulation and semi-capsulation method, the raw powder materials are agitated in a granulator (see Fig. 2.15) by spraying water to bring about agglomerated particles which have bigger size than the original raw materials. Granules were designed to contain self-healing agents inside, a composition of Pozzolan and/or Portland cement and some specific admixtures based on the basic design concept of self-healing proposed by Ahn (2010), coated by an external layer of cement compound and expected to get activated whenever cracking occurs and they become in contact with water [16,19,34]. Fig. 2.16 (a & b) show the difference between the self-healing powders and the final products: granules while Fig 2.16 (c) presents the size distribution of the produced self-healing additives. The size distribution of the proposed granules was similar to standard sand or fine aggregate and, hence, are designed to substitute the fine aggregate while having minimal effect on workability and strength.

Figure 2.15 Pharmaceutical granulator & granulation technique [16,19]



a) With Expansive agents (EG) b) Without Expansive agents



c) Sieve Analysis of Granules

Figure 2.16 Granules with semi-encapsulation effect [16, 19, 34]

Vu (2013) argues that when it comes to the design of granules with semi encapsulation effect, it is important to bear in mind that both self-healing ingredients of granule (term of chemical effect) and granulation technique (term of physical effect) are principal importance to ensure the performance of concrete incorporating granules having semi-capsulation effect. Thus, In order to achieve the granules having semi-capsulation effect, it was proposed that the following materials shown on the Fig 2.17 were used as ingredients for granules [16].

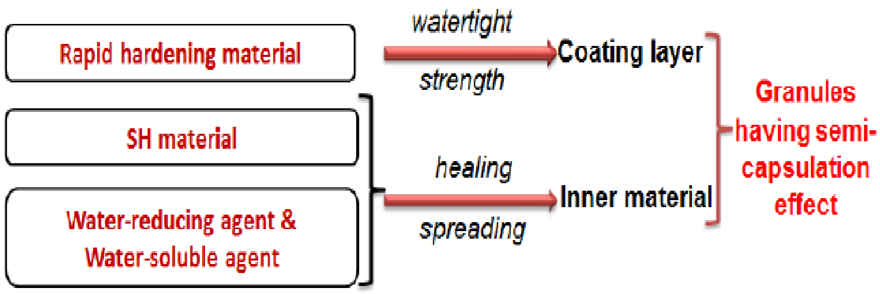


Figure 2. 17 Functional ingredients in granules [16]

Even though the optimum ratio of effective ingredients of granules still were not confirmed yet and it is still difficult to verify the self-healing performance in concrete, the requirements and basic design concepts for granules having semi-capsulation effect were established. The basic ideas are embedded granules should be broken by a penetration of crack and inner self-healing material should be released into crack surface. In order to obtain the targets mentioned above, both requirements of coating layer and inner material should be satisfied simultaneously: coating layer needs to be strong and dense enough; inner material containing reactive agent is weak enough and easy to spread away out of the granule. [16].

It was found that concrete with granules had no adverse effect on the properties of concrete such as the workability of fresh concrete and the compressive strength of hardened concrete; and has a possibility of recovering the water tightness property of cracked concrete, especially in young concrete; and can preserve the healing ability of concrete for a long period of time [16].

On the other hand, having fully spreading efficient granules is expected to be improbable even if granulation technique has minimal impact on fresh properties of concrete. Since during the agglomeration process water is used as a binding agent to manufacture the granules, initial hydration and hardening of the self-healing constituents or the inner materials becomes inevitable. Part of the hydration potential of the granules which could have contributed for the later crack closing process of the concrete is consumed during the granule manufacturing process itself. Similar challenges associated with initial hardening of cementitious granules in self-healing concrete have been reported by Vu (2013). Fig. 2.18 (b) reveals initial hardened state of cementitious granules due to further reactions between cement compound or supplementary cementitious material (main component of inner material) and water used to prepare granules. Because this fact, the strength of granules became high and there was a possibility that granules cannot be ruptured once a crack penetrates into concrete matrix. (see Fig. 2.18 (c)). Another possibility is when ruptured by a crack and exposed to water flow, inner material may not be released into crack surface as the chemical reactions between inner material and flowing water occur inside the granules (see Fig. 2.18 (d)).

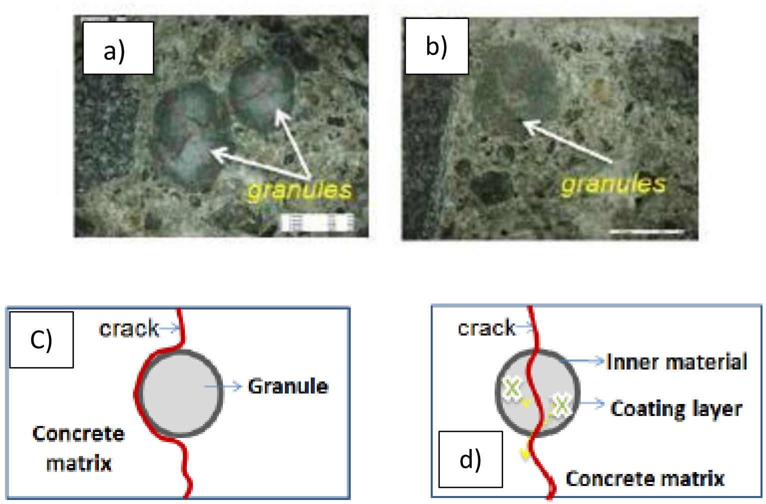


Figure 2.18 Challenges associated with performance of granules (a) large size granules, (b) hardened state of granules (c) problem caused by high strength granule (d) hardened state of inner material [16]

2.4 Chapter Summary

Repairing and maintenance costs involved for concrete structures are usually high. Researches have pointed out that society is investing a huge amount of money for infrastructure maintenance [3]. Self-healing concrete is able to seal off crack routes through which deleterious substances are transported and prolong the service life of structures and minimize the cost of rigorous maintenance. With the target of achieving sustainable infrastructures self-healing concrete, therefore, attracts a lot of research attention as a most promising study scheme.

The phenomenon of self-healing in concrete has been known for many years. It is understood that concrete generally possess an innate self-healing character due to its material components. When water comes in contact with the un-hydrated cement, further hydration occurs. Furthermore, dissolved CO_2 reacts with Ca^{2+} to form $CaCO_3$ crystals. These two mechanisms, however, may only heal small cracks up to 0.1 mm. Low water to cement ratio is expected to promote the natural self-healing potential in concrete since relatively large amount of un-hydrated cement is left in the concrete which is important for autogenous self-healing of cracks.

Based on the understanding of natural ability of concrete to seal off cracks up on contact with water passing through cracks several approaches are being investigated by researchers to design self-healing concrete. Among these approaches the main interest of this research lays in engineered self-healing based on cement based materials and mineral admixtures: a phenomenon in which cracks in concrete are clogged by the use of the concrete made with special material design to close cracks. The balance of various material choices, their effective proportions and the techniques of manufacturing these cementitious self-healing additives with their respective challenges are shortly summarized below.

The simplest form of improving self-healing ability is inclusion of powder type materials. Incorporation of supplementary cementitious materials such as fly ash and blast furnace slag in concrete is reported to result in the improvement of mechanical properties but also to bring about better self-healing capabilities when compared to control samples without these materials. In self-healing concrete made with supplementary cementitious materials, their pozzolanic reaction with $Ca(OH)_2$ from the cement hydration forms a new product similar to hydration products formed filling the crack gap [24, 26-28]. However, for long term cases, researchers have pointed out that $Ca(OH)_2$ may not exist anymore due to carbonation and this fact brings a challenge and the need for more studies to practically apply pozzolanic materials in concrete for self-healing applications [24]. Other studies have suggested the use of expansive agents, mineral admixtures and swelling agents which are capable of expanding, precipitating and swelling and there by filling crack cavities when they come in contact with water [4, 16, 30]. Nevertheless, this technique presented shortcoming of highly affecting the mixture workability. And the powder type self-healing additives are directly added into the concrete mixtures without any protection, once they come in contact with water during the mixing of concrete, they immediately start to react. As a result, these added materials are expected to be consumed before cracking.

Later the granulation and semi capsulation approach was introduced to overcome the drawbacks of the powder approach. In this method, the raw powder materials are agitated in a granulator by spraying water to bring about agglomerated particles which have bigger size than the original raw materials. Granules were designed to contain self-healing agents inside, a composition of Pozzolan and/or Portland cement and some specific admixtures and coated by an external layer of cement compound and expected to get activated whenever cracking occurs and they become in contact with water [16,19]. It was found that concrete with granules had no adverse effect on the properties of concrete such as the workability of fresh concrete and the compressive strength of hardened concrete; and has a possibility of recovering the water tightness property of cracked concrete, especially in young concrete [16,19,34]. On the other hand, having fully spreading efficient granules is expected to be improbable even if granulation technique has minimal impact on fresh properties of concrete. Since during the agglomeration process water is used as a binding agent to manufacture the granules, initial hydration and hardening of the self-healing constituents or the inner materials becomes inevitable.

CHAPTER 3 METHODOLGY

3.1 Introduction

This chapter describes in detail the methods and experimental set ups of water pass tests followed in this research as evaluation of self-healing recovery. Several trials of mortar were cast having two types self-healing additives. The first type of additives were powder compacted aggregates to be discussed in chapter 4 while the second type of self-healing additives were cement granules prepared with coating liquid and to be described in chapter 5. For sake of comparison control mortar specimen without additives replacing the sand are prepared in each of the trials.

3.2 Mortar casting and curing

3.2.1 Materials for mortar

Ordinary Portland cement of Type I Japan Portland cement with density of 3.15 g/cm^3 was used in all mortar mixtures. Fujigawa river sand with surface dry density of 2.62g/cm^3, absorption of 2.1% was used for making the tested mortar mixtures. The particle size of the sand was less than 4.75 mm and the FM was 2.55.

3.2.2 Mixing composition and procedures

Table 3.1 presents the mix proportion of the mortar which were prepared according to JIS R 5201 procedures. The self-healing additives replaced the sand partially at a dosage rate of 60 and 120 kg/m^3 of mortar. Measurement of flow values and air content were conducted for each mixes according to the procedures in JIS R 5201.

Table 3.1 Mortar mix design

w/c	Unit weight (Kg/m^3)				Designation
	Water	Cement	Sand	Self-healing additive	
0.5	264	528	1345	0	Control
			1285	60	A
			1225	120	B

All the specimen are then kept in sealed condition (see Fig 3.1) at 20^0C until the compressive strength and water pass tests proceeded. The compressive strength was measured by universal testing machine at a loading rate of 1.5 KN/min for sealed cured mortar specimen at the age of 7, 28 and 91 days.

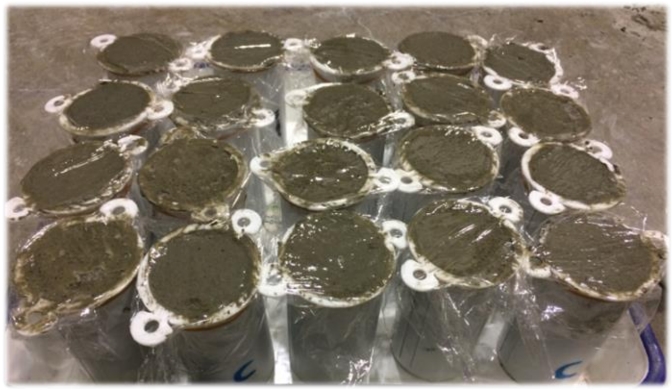


Figure 3.1 Mortar specimens sealed curing

3.3 Water pass test procedures

3.3.1 Specimen preparation

In order to estimate the self-healing ability water pass test for mortar is conducted on 28 days old or 91 days old sealed cured specimen; the methodology of which will be explained in detail below. The water flow tests were conducted according to the proposal of Morita (2011) and later by Vu (2013) for conducting water flow measurements [16].

The specimen were first cracked longitudinally by splitting test; v-notches are used to transfer the load from the Universal testing machine to the specimen to longitudinal straight lines. (see Fig. 3.2). The surfaces are then cleaned with brush to remove broken particles. Teflon sheet strips were then introduced on the surface of the crack to provide average crack widths of 0.2 and 0.3 mm (see Fig. 3.3). Teflon sheets are added along crack surface to maintain efficient water flow distribution within the crack opening. Next, the closed specimen were fixed by using hose clamps. Three points were marked with ink at the bottom surface of the specimens (see Fig 3.4).

Figure 3.2 Cracking specimen into halves using V-notches

Figure 3.3 Provision of Teflon sheets on crack surface

Figure 3.4 Tying back specimen halves and marking of the bottom surface

After the specimen halves are closed back, measurement of bottom crack width using microscope under X100 magnification was done to determine the average crack width (see Fig 3.5 a). Crack width measurements are done at three random points for each three marked points (see Fig 3.5 b).Therefore; the average crack width is estimated as a mean of nine measurements. Whenever the average crack width showed a difference of 50 µm or more from the desired crack width adjustments were done to bring it to the allowable range of ± 50 µm.

After confirmation of the average crack width by microscope, the specimen boundaries are closed by using silicone adhesive. PVC pipe is fit using the adhesive at the top of the specimen to maintain a constant head of 4 cm (see Fig 3.6).

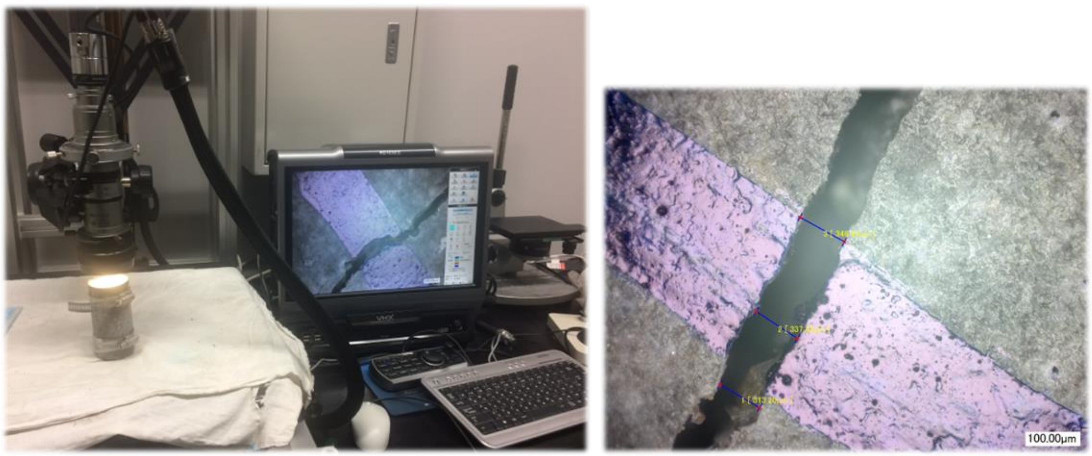


Figure 3.5 Measurement of bottom surface crack width by microscope (a) Crack width measurements along three random points around the markings (b)

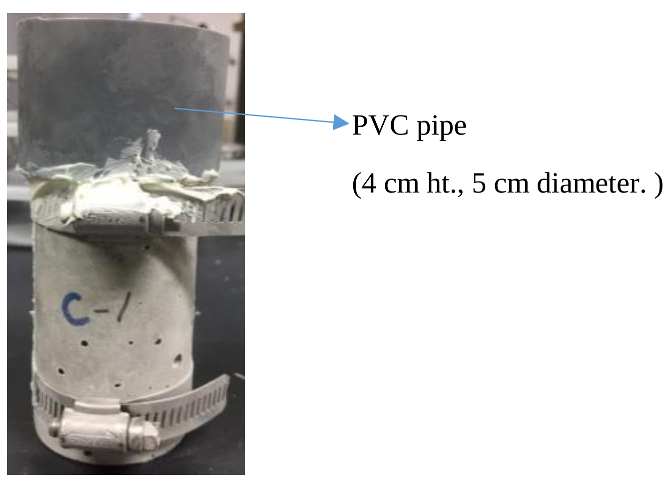


Figure 3.6 Specimen after closing the boundaries and fixing PVC pipe

3.2.1 Water flow measurement procedures

There are several self-healing efficiency measurement methods and there is no singly and widely adopted self-healing test yet. Water flow measurements are adopted as one way of checking the self-healing recovery in a relatively faster time. In this approach, a falling head or a constant head is used to examine the extent of self-healing by monitoring the flow rate or quantity of water passing through cracked specimens. The change in the rate of water flow with respect to time is used to measure the amount of healing which has occurred. Typically a rapid fall in flow value followed by a gradual reduction is used to infer self-healing taking place in the specimen (see Fig. 3.7).

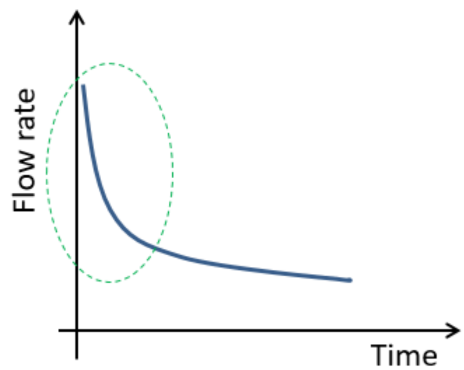


Figure 3.7 General trend of water flow test results

This approach of testing is restricted to describing crack sealing by continued cement hydration product formation and requires the promotion of self-healing derive from water which may carry dissolved CO_2 flow through the crack. Formation of calcite in the crack has been cited as a reason for increase of sealing function over time [10-13]. The early research on self-healing of concrete mainly focused on water retaining structures or reservoirs where leakage through cracks was the main issue. Self-healing of cementitious materials is said to occur due to several of the following mechanisms in such cases as suggested by past researchers [10-12,16].

> Continued hydration: Cement hydration persists for long period of time depending on the availability of water in the cement matrix. On cracking and upon contact with water unhydratred cement particles may continue to form hydration products bringing about crack closure.

Formation of Calcite: Cement hydration is known to result in $Ca(OH)_2$. This compound may react with atmospheric CO_2 or CO_2 dissolved in water to result in calcite formation. Then, the precipitated carbonate deposits on crack surface and crack closure results.

Sedimentation of particles with in crack spaces: On cracking concrete produces small constituent particles that may be moved along the flowing water. Combination of such particles and impurities in water may contribute to crack closure.

Swelling of the cement matrix: Ingress of water into cementitious materials may cause swelling resulting from water saturation and this can cause crack closure.

These above mentioned mechanisms of self-healing have come to question when it comes to their contribution to early stage water flow reduction. Recent verifications by Ikoma et.al. (2015) showed that these primarily known mechanisms show only limited effect on the initial water flow reduction. Observations were conducted in the study on half crack surface concrete specimen with glass or an acrylic resin to stimulate the surface characteristics of the opposite crack side. Through water flow through the interfaces with the use of colored and videography, it was revealed that the generation and growth of air bubbles takes place (see Fig. 3.8) narrowing the water flow space and decreasing the flow values at early stages [35-37].

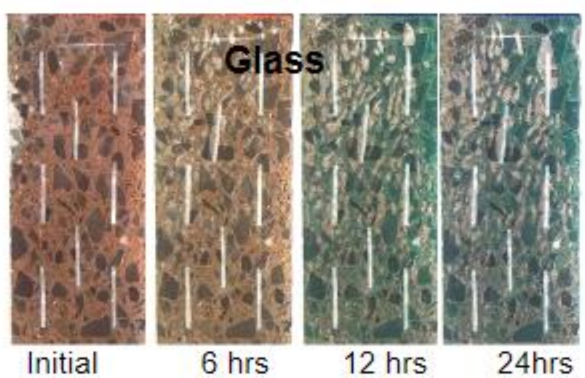


Figure 3.8 Air bubbles observed through concrete-glass interface [35]

Kayondo & Kishi (2016) pointed out that the formation of large air bubbles on crack surfaces will not occur when less than 100% air saturated water was used for water pass tests (see Fig 3.9) [37]. Therefore, equilibrated water having an average DO content less than 95 % was utilized for conducting all water pass tests in this study to avoid the influence of large air bubbles on the water flow measurements.

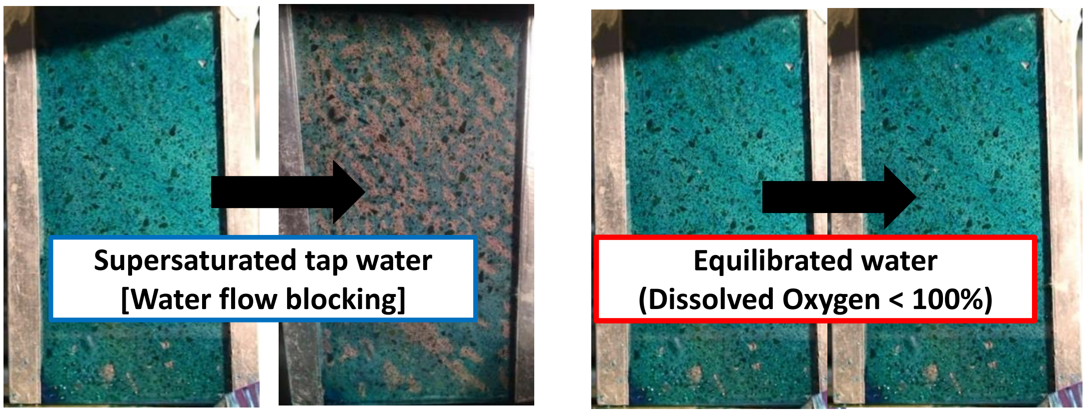


Figure 3.9 Observation of air bubble formation with tap and equilibrated water [37, 38].

Based on the above back grounds of air bubble effect and its growth mechanisms, proposal of graded estimation scheme was presented by Kishi (2017). The necessary requirements for 1st step water pass test for inferior grade are listed as follows;

- **Initial curing: 1 month** – minimize active hydration
- Periodical instantaneous water pass test with equilibrated water **(Dissolved Oxygen: 95-100 %)**
- Keep in **static water** between water pass tests
- **Quick sealing** must be verified in a week

In the experiment study, in order to remove any trapped air bubbles with in the specimen, initial vacuum soaking was suggested by a previous study before starting water flow measurements [37]. After the silicone was dried, the prepared specimen were thus put in vacuum chamber at a suction pressure of 60 cm of Hg in dry condition for 3 hours. After that water was supplied and the specimen were kept wet soaked in vacuumed condition for 24 hours. This procedure is adopted as a close approximation of the JSCE standard which recommends the samples be vacuumed under dry condition at the pressure lower than 150 Pa for 3 hours and supplying water under vacuumed condition and soaking the sample for one hour. As a last step of the JSCE procedure, the vacuum is released and the specimens are kept under water for 24 hour.

Figure 3.10 Vacuuming of specimen in vacuum chamber

In similar water flow tests where water having equilibrated dissolved air content was used it was possible to continue water flow reduction. The main difference was this time no noticeable air bubble growth was observed. However, the water flow reduction was observed regardless of the absence of visible air bubble later confirmed to be due to the presence of micro and nano air bubbles fixed to the material surfaces [37, 38]. At the end of the 14th, 28th and 56th day of water pass tests, secondary vacuum soaking was conducted (in addition to the initial vacuum soaking) following the same procedures as the initial one, to exclude effect of invisible air bubbles on the measured water flow.

As final stage, water flow rates were recorded as a means of quantifying the self-healing capability of the specimens. Fig. 3.7 presents the water flow measurement set-up used in the study. Three specimen were used per trial and average weight of the water collected in 5 minutes were recorded. Water flow rates were then computed as;

$$Water\ flow\ rate\ (\frac{gm}{sec}) = \frac{\text{Weight 5 min}}{300} \quad (3.1)$$

Where Weight 5 min is the weight of equilibrated water in grams collected at any given measurement period.

The water flow measurements were done at every day for the 1st seven days and at 10th, 14th, 21st, 28th and 56th day. Besides measurement of weight of water collected at every measurement interval, the pH of the static water container where specimen are stored is measured using pH water.

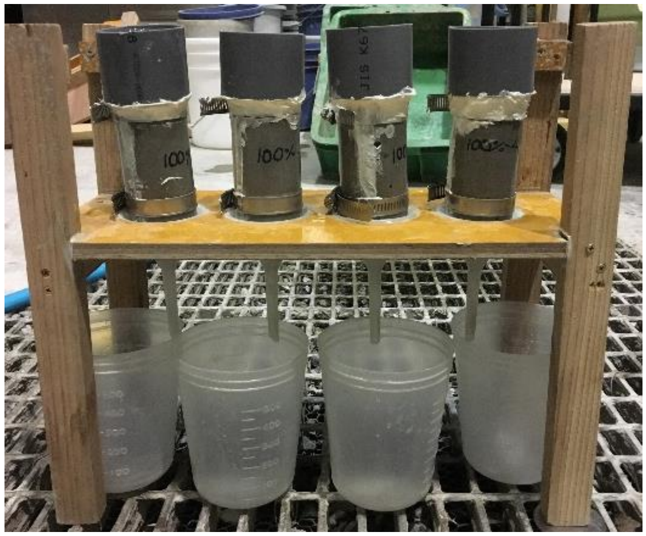


Figure 3.11 Water flow measurement setup

3.4 Evaluation of water pass test results

In the experimental study, at the end of the 14^{th}, 28^{th} and 56^{th} day of water pass tests, secondary vacuum soaking was conducted (in addition to the initial vacuum soaking) following the same procedures as the initial one, to exclude effect of invisible air bubbles on the measured water flow. The flow rate values computed by equation 3.1 are then compared for the initial 0 day flow and the values at each period before vacuuming and after vacuuming. Equation 3.2 below presents the computation of the flow reduction in percent;

$$Flow\ reduction\ (\%) = \frac{f\ 0day - f\ nth\ day}{f\ 0\ day}\ X\ 100 \quad \text{.......................................} (3.2)$$

Where f_{0day} is the water flow rate at 0 day of water pass test,

$f_{nth\ day}$ is the water flow rate at the 14^{th}, 28^{th} or 56^{th} day of the test

The average of the flow reduction for three specimen after vacuuming is adopted as a way to measure the crack closing by solid products formation. In reality, however, crack closure is understood to be caused by the combined effect of flow blocking by visible and invisible air bubbles as well as solid crystallization and deposition.

3.5 Summary of water pass test procedures

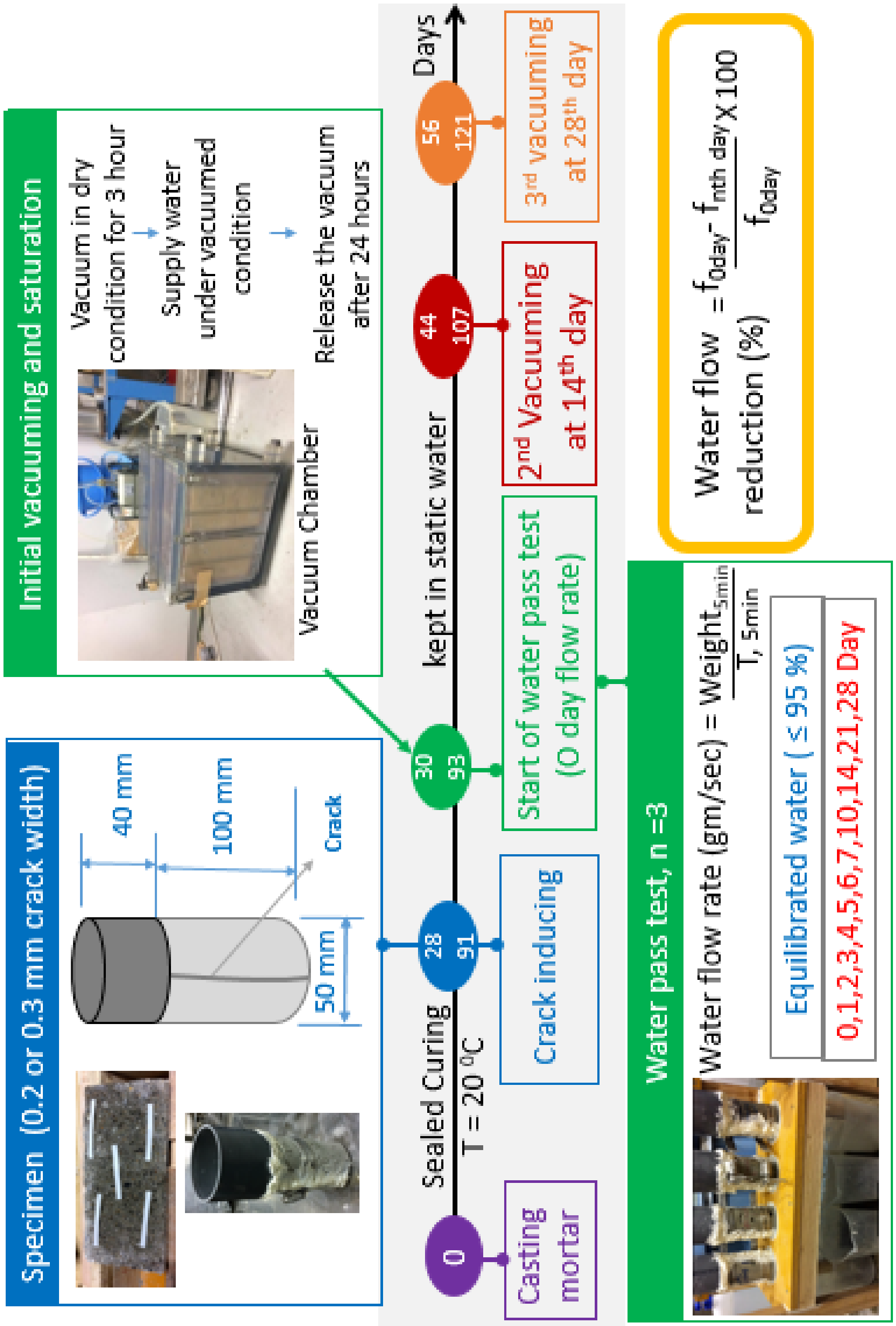


Figure 3.12 Summary of the water pass test procedures followed in the study

CHAPTER 4 APPLICATION OF POWDER COMPACTED AGGREGATES TO CRACK SELF HEALING MORTAR

4.1 Powder Compaction of cementitious materials

Powder compression is defined as the reduction in volume of a powder owing to the application of a force. Because of the increased proximity of particle surfaces accomplished during compression, bonds are formed between particles which provide coherence to the powder, i.e. a compact is formed. Compaction is defined as the formation of a solid specimen of defined geometry by powder compression [39].

In the first stage of powder pressing density is increased by a rearranging of the individual powder particles. Spaces, bridges and gaps are eliminated, and density increases due to a more efficient packing of the particles. This initial stage provides relatively lower resistance and the density of the powder increases with applied pressure. Contact points between particles become established. As compression increases, increasing forces act between these contact points [40].

4.1.1 Bonds formed by compaction

The dominating technique of forming tablets in pharmaceutical industry is by powder compression, i.e. forcing particles into close proximity to each other by confined compression. This enables the particles to cohere into porous, solid tablets of defined geometry and weight [39]. The same unit operation with different types of powders is equally essential in powder metallurgy and structural ceramics production.

The transformation of a powder into a tablet is fundamentally an interparticulate bonding process, i.e. the increased strength of the assembly of particles is the result of the formation of bonds between them. The nature of these bonds is traditionally subdivided into five types, known as the Rumpf classification;

1. Bonding by liquids (capillary and surface tension forces)

2. Solid bridges

3. Binder bridges (viscous binders and adsorption layers)

4. Intermolecular and electrostatic forces

5. Mechanical interlocking

The first type of bonds is originated from the presence of liquids such as water and /or alcohol that are dripped, sprayed or poured into a shearing mass of powder. The granulating fluid can typically composed of water and/or alcohol and may contain surfactants and Polymers. Despite the complexity, an accepted view holds that the liquid binder wets and spreads in the interstices between primary particles, forming liquid bridges that hold them together by capillary and viscous forces. These wet granules are subsequently dried, and liquid evaporates from the bridges to leave behind solid bridges or necks that impart mechanical strength to the dry granule. The process of solid bridge formation from liquid bridges between particles is not unique to granulation and in fact plays a significant albeit unwanted role in powder caking. Additionally, solid bridges also referred to as the diffusion theory of bonding, can occur when two solids are mixed at their interface and accordingly form a continuous solid phase. Such a mixing process requires that molecules in the solid state are movable, at least temporarily, during compression. An increased molecular mobility can occur due to melting or as a result of a glass-rubber transition of an amorphous solid phase [39, 41].

When binder–substrate granules are compacted, it is assumed that the binder plays the most important role in the formation of intergranular bonds. The binder may fuse together locally and form binder bridges between granule surfaces which cohere the granules to each other. Such bridges may be the result of a softening or melting of binder layers during the compression phase. According to Aulton (2013) different types of adsorption bonds may be active between granule surfaces which are subdivided into binder–binder, binder–substrate and substrate–substrate bonds [39].

Bonding by intermolecular forces is sometimes also known as adsorption bonding, i.e. the bonds are formed when two solid surfaces are brought into intimate contact and subsequently adsorb to each other. Among the intermolecular forces, dispersion forces formed by movement of electrons and the resulting slight polar moments are considered to represent the most important bonding mechanism. This force operates in a vacuum and in a gaseous or liquid environment up to a separation distance between the surfaces of approximately 10–100 nm [39].

Mechanical interlocking is the term used to describe a situation where strength is provided by interparticulate hooking (See Fig. 4.1). This phenomenon usually requires that the particles have a typical shape, such as needle-shaped, or highly irregular and rough particles. According to Aulton (2013), in the case of compaction of dry powders without the use of liquids, two of the suggested types of bond are often considered to dominate the process of interparticulate bond formation, i.e. bonding due to intermolecular forces and bonding due to the formation of solid bridges.

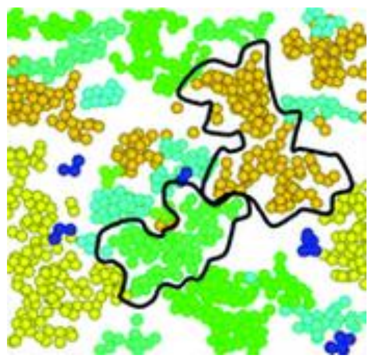


Figure 4.1 Mechanical interlocking [45]

4.1.2 Hydrated cement powder compaction

Soroka and Sereda (1970) reported that when hardened cement paste is crushed and pressed, it was capable of forming solid compact. The hardness and modulus of elasticity of the cement stone formed by powder compaction was found out to be the same as that of the original cement paste before crushing when the total pore volume was kept the same (see Fig. 4.1). The amount of the applied pressure varied from 140 to 1123 MPa to make compacts with levels of porosity varying between 25 to 60%. The research, in addition, involved using plaster of Paris ($CaSO_4.1/2H_2O$) which hydrates to give gypsum. It was observed that plaster of Paris molded into bodies and allowed to hydrate produces a higher modulus of elasticity at a given porosity than solids made from compacted, prehydrated gypsum (see Fig. 4.2).

From the observations, it was suggested that the strength of the cement paste stone is mainly derived from a particular type of inter-particle bond. It was concluded that the Tobermrite sheets, forced in to proximity, might make a connection composed of van der Waals forces, the relative amount depending on the degree of matching of the lattice. The gypsum system known to develop strength by intergrowth of crystals was considered to have reduced Young's modulus value as the crystal bonds are partly broken in compacted cast gypsum [42].

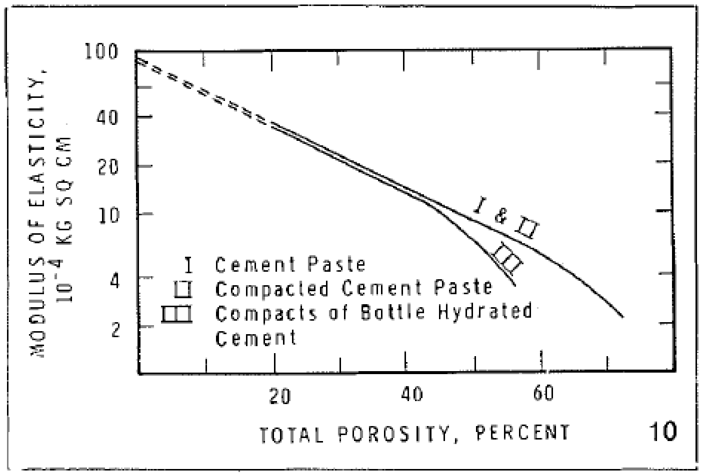


Figure 4.2 Young's modulus vs porosity relations for various hydrated cement specimens [43]

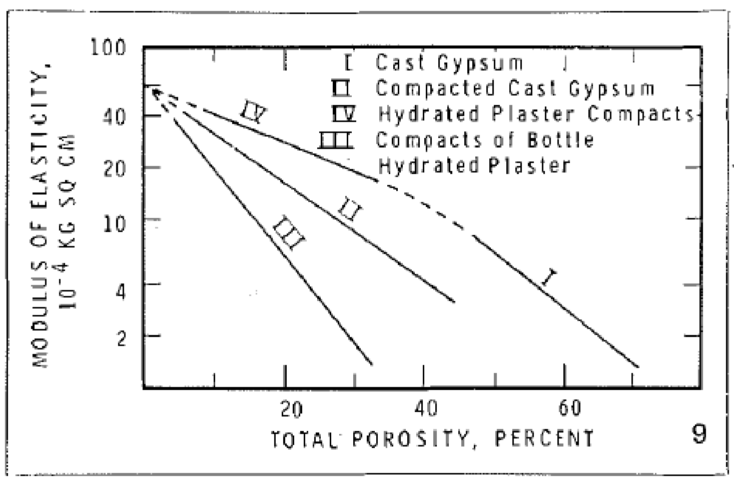


Figure 4.3 Young's modulus vs porosity relations for various gypsum specimens [43]

4.1.3 Powder compaction as recycling method for waste concrete

A related study on powder compaction was done by Sakai (2014) in an effort to utilize the method for complete recycling of concrete with in short duration of time. Fig. 4.4 presents the compressive strengths of compacts formed from mixtures of aggregate and hydrated cement paste powder with different paste volume ratios. A unidirectional pressure of 200 MPa was used to prepare the solid compacts from powders of 200 μm maximum size. According to the study, the compressive strength of the compacts linearly increased with the cement paste volume up to 80%.

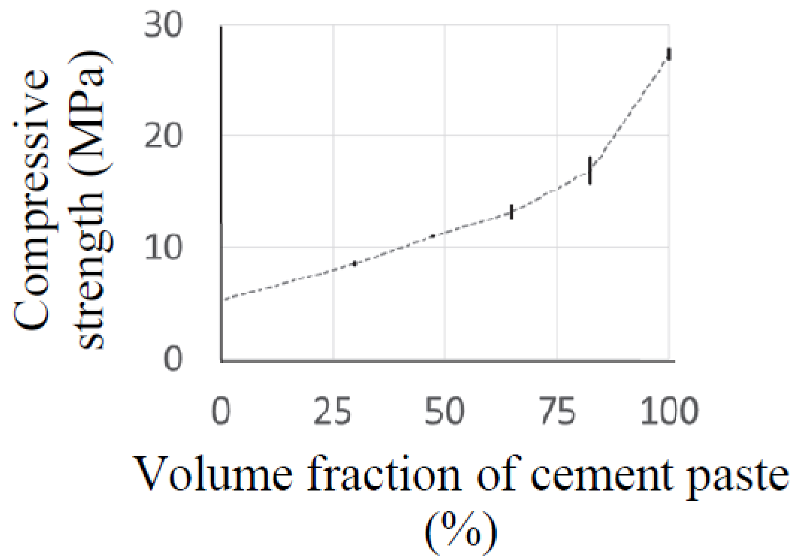


Figure 4.4 Compressive strength of mixtures of aggregate and hydrated cement paste powder [44]

Concrete powder compaction, which lies between the two extremes of pure aggregate hardened cement powder compaction, showed three times less than that of the compacts of cement paste. Thus, as a measure to raise the reduced compressive strength of powder compacted concrete, Sakai (2014) suggested partial replacement of the concrete powder mass by cement powder or sludge powder which is a byproduct of concrete mixing plants. Fig. 4.5 shows the compressive strength of crushed and compacted hardened concrete formed by unidirectional compaction pressure of 200 MPa maintained for 10 minutes. Fifty percent replacement with hydrated cement paste powder and sludge powder was shown to effectively improve the compressive strength of the formed concrete. Moreover, accelerated carbonation treatment of the formed compacts done by placing the specimens in a container filled with CO_2 gas for 48 hours has improved the strength by the largest degree (see Fig. 4.5).

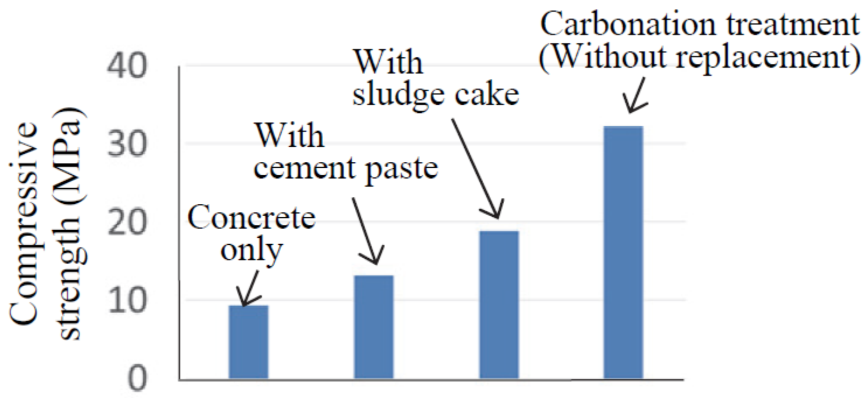


Figure 4.5 Compressive strength of crushed and compacted hardened concrete under different conditions [44]

4.2 Preparation of Powder Compacted Aggregate (PCA)

4.2.1 Materials

(1) Ordinary Portland cement

Type I Japan Portland cement with density of 3.15 g/cm^3 was used in all PCA

(2) Fly ash (FA)

JIS A 6201:2008 fly ash fine powder for concrete having density of 2.21 g/cm^3 and Blain fineness value of 3400 cm^2/g was used for preparing PCA.

(3) Blast furnace slag (BFS)

JIS A 6206:2013 blast furnace slag fine powder for concrete was used for preparing PCA. The BFS has a density of 2.91 g/cm^3 and Blain fineness value of 4250 cm^2/g.

(4) Sludge powder

Liquid sludge resulting from ready-mix concrete plants is a waste from washout of concrete mixing trucks (See Figure 4-6 and Figure 4-7). This waste water derived from the concrete mixing plants is hazardous for disposal due to its high alkalinity caused by the hydration reaction of cement. Even if there is no one universal way of recycling the sludge, some concrete mixing factories filter the liquid sludge and reuse the clean water for mixing concrete after neutralization.The dehydrated sludge cake is then stored after air for drying (Figure 4-8) and reduction of its volume. This filtered air-dried sludge cake was sampled from Tokyo - SOC Share Company in Chiba prefecture, Japan.

Sludge powder was prepared by crushing and milling the sludge cake sample after drying it at 40 ^{0}C for 24 hours. The moisture content of the sludge cake after drying at 40 ^{0}C chamber was 12.1 %. To measure the moisture content, a 20 gram powder sample was heated in an oven at 105 °C. Here, the moisture content is calculated by dividing the weight change due to heating by the weight after heating in oven. Sludge powder that passed through a 105 µm sieve was collected for preparing PCA. Fig 4.9 summarizes the steps that led to the preparation of sludge powder sample. After the powder is prepared it is kept in plastic bags zipped in airtight condition to avoid contact with atmospheric moisture.

Figure 4.6 Washout of truck mixer

Figure 4.7 Liquid sludge well

Figure 4.8 Air drying of sludge cake

(a) (b)

(c) (d) (e)

Figure 4.9 Sludge powder preparation (a) sludge cake (b) drying in constant temperature chamber (c) crushing by jaw crusher (d) grinding by electrical blender (e) sieving (105 µm)

(5) Coating liquid (CL)

In this research, Polyethylene Glycol 400 (PEG 400) was used as coating liquid (CL) to protect cement particles from reaction during mixing and to temporarily preserve them until they become in contact with water when crack opens at later matured stages. PEG 400 is a low-molecular-weight grade of polyethylene glycol. It is a clear, colorless, viscous liquid that is widely used in a variety of pharmaceutical formulations. PEG 400 is soluble in water, acetone, alcohols, benzene, glycerin, glycols, and aromatic hydrocarbons, and is slightly soluble in aliphatic hydrocarbons.

4.2.2 Method of forming the PCA

Powder compacted aggregate (PCA) were prepared by crushing and sieving powder compacts manufactured according to the steps followed by Sakai et.al. (2015) [7].For producing compacts, four series of powder mixtures were prepared initially based on the proportion of the self-healing powder materials (OPC, FA & BFS) and sludge powder (see Table 4.1).

Figure 4.10 Mixture of powders (Sludge and OPC)

Next, the preparation of the compacts was conducted by unidirectional loading of universal testing machine. In the unidirectional pressing, a set of steel molds with cylindrical cavities of 50 mm in diameter and 170 mm in height was used. The prepared self-healing powder mixture was then poured into the cylindrical cavity. The consolidation stress in the universal testing machine is then gradually applied by steel cylinder with diameter of 50 mm (see Fig. 4.11) while the maximum forming pressure is maintained for 1 minute to form the compacts. The compact formation pressure is defined as the applied load divided by the cross-sectional area of the compact. In order to make samples with different strength, the applied pressure is varied as 10 or 25 MPa. 10 MPa was the minimum pressure required to form solid compacts. Fig. 4.12 presents the formed powder compacts of 50 mm diameter after taking them out of the mold.

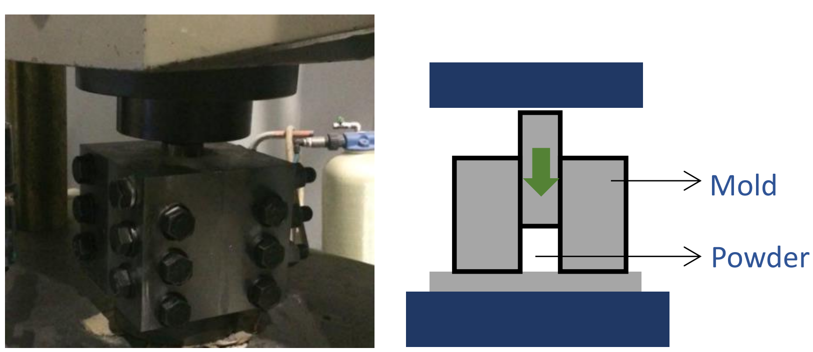


Figure 4.11 Application of compact formation pressure by UTM

Table 4.1 Formation pressure and mixture composition of PCA

Group	Designation	Compact formation pressure (MPa)	Mix proportion by weight (%)				Coating liquid absorption ratio by wt.
			Sludge powder	OPC	FA	BFS	
1	PC1_1	10	30	50	20		0.245
	PC1_2	25					
	PC1_3	10				20	0.233
	PC1_4	25					
2	PC2_1	10	30	35	35		0.2585
	PC2_2	25					
	PC2_3	10				35	0.2375
	PC2_4	25					
3	PC3_1	10	30	70			0.227
	PC3_2	25					
4	PC4_1	10	50	50			0.245
	PC4_2	25					

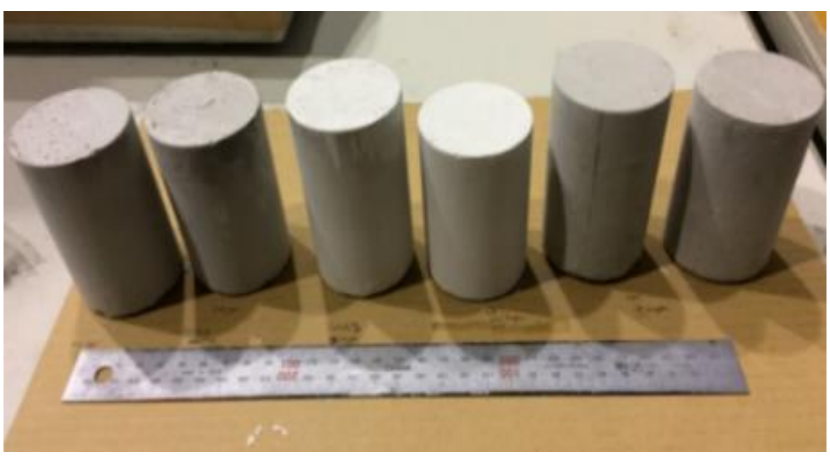


Figure 4.12 Powder compacted samples

The formed powder compacts were crushed using mechanical jaw crusher and sizes passing 1.18 mm sieve size were used as self-healing additives partially replacing sand/fine aggregate/ in mortar hence given the name powder compacted aggregate. The mean diameter of the PCA was 300 µm. The PCA were then saturated by the coating liquid to protect them from immediate contact with water during mortar mixing process. Coating liquid absorption rate of PCA (see Table 4.1) was calculated by keeping 50 gm powder compacts in the coating liquid for 24 hours and dividing the weight change after dipping to the original weight. Fig. 4.15 shows PCA samples after crushing and saturating them with coating liquid.

Figure 4.13 keeping the powder compacts in coating liquid

Figure 4.14 Crushed powder compacts before sieving

Figure 4.15 Powder Compacted Aggregate after sieving and saturation with coating liquid

Figure 4.16 Storage of the Powder Compacted Aggregate until mixing

4.2.3 Gradation of the PCA

Figure 4.16 present the particle size distributions of the manufactured PCA compared to standard fine aggregate after sieving by 1.18 mm sieve, the self-healing additives partially replacing sand/fine aggregate/ in mortar. The manufactured PCA had size distributions much less than sand with mean diameter of 300 µm. Finer size PCA are prepared to assure well distribution of the self-healing additives throughout the self-healing mortar mixes.

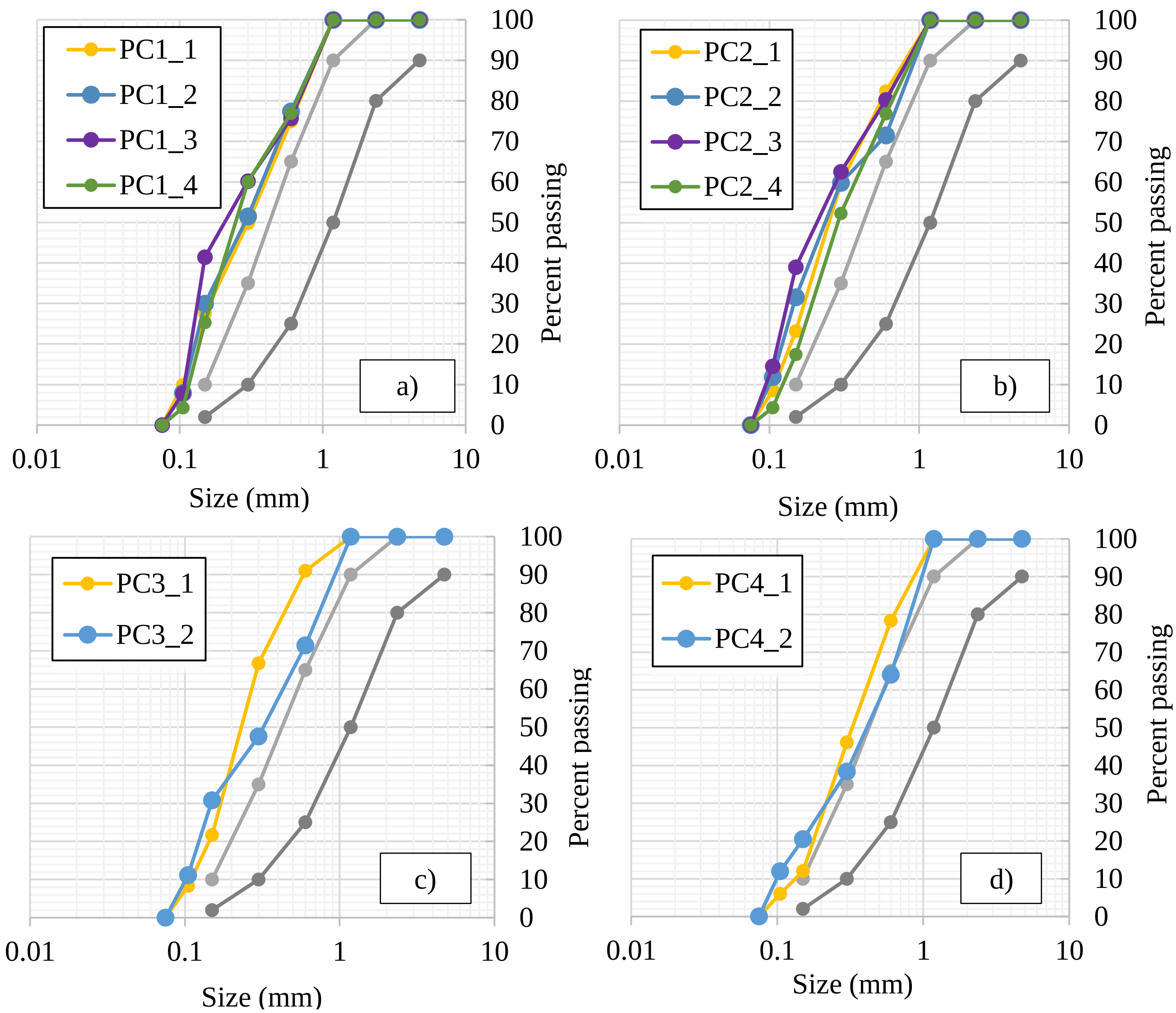


Figure 4.17 Gradation of the PCA (a) Group 1 (b) Group 2 (c) Group 3 (d) Group 4

4.3 Preparation of powder type of additives

Table 4.2 presents the mix proportions of powder types of additives prepared to be added to self-healing mortar as sand replacement. These are used to make binary mixes as comparison to estimate the additional advantage that can be obtained by compaction of the powders and including them as powder compacted aggregates for self-healing.

The powder type additives are saturated by the coating liquid to protect them from immediate contact with water during mortar mixing process. Coating liquid absorption rate of the prepared powders (see Table 4.2) was calculated by keeping 50 gm powder compacts of same composition for 24 hours and dividing the weight change after dipping to the original weight. Fig. 4.17 shows the powder type additives after saturating them with coating liquid.

Table 4.2 Mix proportions of powder type additives

No.	Designation	Coating liquid absorption ratio by wt.	Mix proportion by weight (%)				Notes
			Sludge powder	OPC	FA	BFS	
1	Slc	0.29	100				Crushed sludge (100-1000 μm)
2	Slf	0.29	100				Crushed sludge (<105 μm)
3	Op	0.2		100			
4	Fp	0.29			100		
5	Bp	0.23				100	
6	OFp	0.22		80	20		OPC + FA
7	OBp	0.206		80		20	OPC + BFS

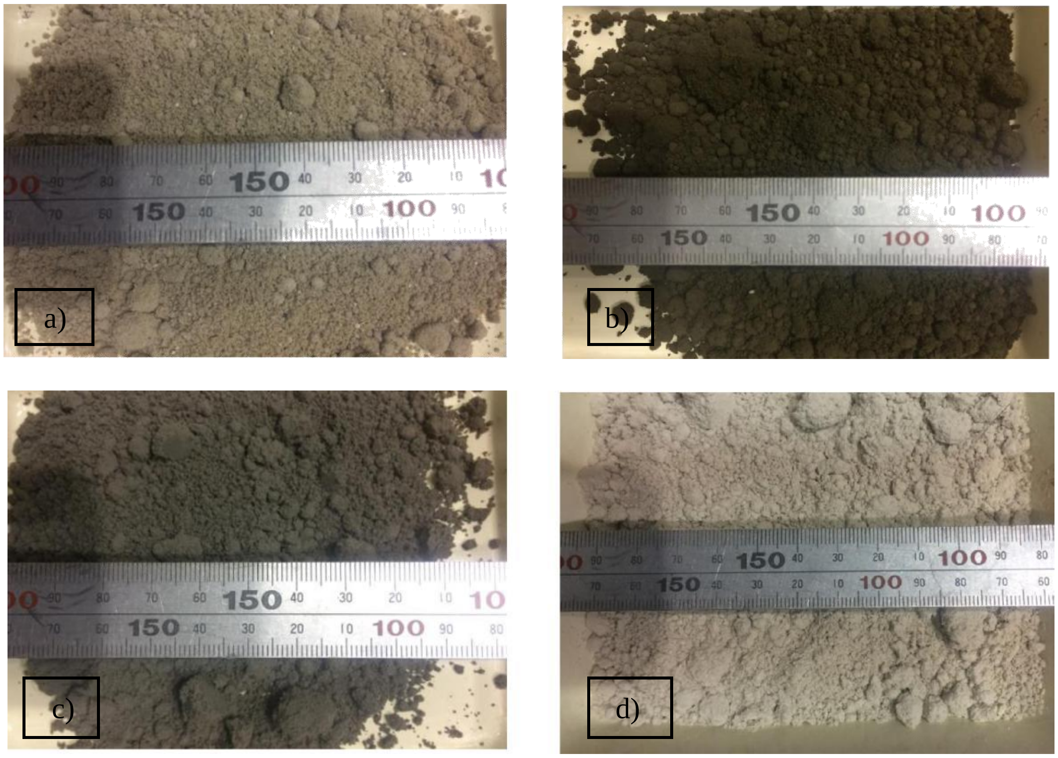


Figure 4.18 Powder type additives (a) sludge powder (b) OPC (c) FA (d) BFS

4.4 Effect of PCA and powder type additives on fresh and hardened properties of Mortar

4.4.1 Fresh properties of mortar mixes with PCA and powder type additives

Table 4.3 presents the mix proportion, the measured air content and the zero drop flow values of the self-healing mortar prepared by adding PCA as sand substitutes and control specimen. The mortar designated with A at the end of the name represent samples with 60 Kg/m^3 dosage of PCA and those with B represent 120 Kg/m^3 dosage of PCA. The air content for the mortar mixes with powder compacted aggregates right after casting is conducted according to the guidelines of JIS A 1128, method of test for fresh concrete by pressure method. It can be seen from the results that the enclosure of PCA in to the mortar mix caused increment in the air content by up to 2.4% when compared to the control mix which had no PCA substituting the sand (see Table 4.3). The maximum air content difference of 2.4 % was exhibited by PC2_1B. The observed rise in the air content values was generally proportional to the PCA dosage; the higher the dosage the higher the air content. The possible reason for increment in air content could be the presence of the coating liquid that is used to saturate the PCA.

Table 4.3 Mix composition and fresh properties of mortar formed with PCA

Mortar designation	PCA group	PCA type	Unit weight (Kg/m^3)				Fresh property	
			w	C	S	PCA	Air (%)	Zero drop flow (mm)
Control	-	-	264	528	1345	-	3.5	77
PC1_1A	1	PC1_1			1285	60	3.6	78
PC1_1B					1225	120	5.1	80
PC1_2A		PC1_2			1285	60	4.7	80
PC1_2B					1225	120	5.4	89
PC1_3A		PC1_3			1285	60	4.9	82
PC1_3B					1225	120	5.8	95
PC1_4A		PC1_4			1285	60	5.2	86
PC1_4B					1225	120	5.7	91
PC2_1A	2	PC2_1			1285	60	5.3	81
PC2_1B					1225	120	5.9	93
PC2_2A		PC2_2			1285	60	4.6	80
PC2_2B					1225	120	5.5	93
PC2_3A		PC2_3			1285	60	4.1	77
PC2_3B					1225	120	4.8	90
PC2_4A		PC2_4			1285	60	4.6	81
PC2_4B					1225	120	5.8	95
PC3_1A	3	PC3_1			1285	60	5.3	82
PC3_1B					1225	120	5.5	90
PC3_2A		PC3_2			1285	60	4.7	78
PC3_2B					1225	120	5.1	90
PC4_1A	4	PC4_1			1285	60	3.9	77
PC4_1B					1225	120	5.5	91
PC4_2A		PC4_2			1285	60	4.0	74
PC4_2B					1225	120	5.1	89

Table 4.4 Fresh properties of mortar with powder type of additives

Mortar designation	Self-healing additive	Unit weight (kg/m^3)				Flow (mm)	Air content (%)
		W	C	S	Self-healing additive		
Control	-	264	528	1345	0	77	3.5
Slc_A	Slc			1285	60	74	4.5
SlC_B				1225	120	79	5.7
Slf_A	Slf			1285	60	77	5.1
Slf_B				1225	120	79	5.5
Op_A	Op			1285	60	84	4.9
Op_B				1225	120	91	5.6
Fp_A	Fp			1285	60	90	5.2
Fp_B				1225	120	94	6.1
Bp_A	Bp			1285	60	86	3.9
Bp_B				1225	120	91	5
OFp_A	OFp			1285	60	82	4.6
OFp_B				1225	120	90	5.3
OBp_A	OBp			1285	60	87	5.1
OBp_B				1225	120	93	5.8

Accordingly, it could be pointed out that consideration of the air content design should be taken care of if there are tight tolerances when using PCA. Most concrete mix design guidelines allow a variation of ± 1 % from the target air content of concrete mixes. According to the results for the mortar samples with PCA which showed a maximum difference of +2.4 % from the control could be considered as mild effect that needs to be addressed during the initial mix design stage. The effect of the PCA at dosage rate of 60 Kg/m3 on the air content, however, is within the acceptable limit of ± 1 % difference compared to compared to the control for most of the self-healing mixes (see Table 4.3).

The zero drop flow values for the mortar with PCA are measured immediately after casting following the JIS R 5201 guidelines and the results are shown in Table 4.3. The experimental results show that the mortar flow values at PCA dosage rate of 60 Kg/m3 were mostly slightly higher than the measured flow of the control sample. Among the A type samples with 60 Kg/m3 dosage of PCA the maximum flow of 82 mm was observed for PC1_3A, while the minimum flow 74 mm was exhibited by PC4_2A.

At higher PCA content of 120 Kg/m3 the zero drop flow values showed increment of values up to 18 mm compared to the control mix (see Table 4.3). Therefore, addition of PCA to mortar can be one approach to overcome drawback of reduction of workability that takes place when incorporating self-healing materials in their raw powder form. This increment in flow values is likely due to the presence of the coating liquid used to saturate the PCA and related changes in fluid content with in the mix.

Table 4.4 presents the mix proportion, the measured air content and the zero drop flow values of the self-healing mortar prepared by adding powder type additives and control samples. The mortar designated with A at the end of the name represent samples with 60 Kg/m3 dosage of powder type additives and those with B represent 120 Kg/m3 dosage of powder type additives. Compared to the control sample the air content values of the self-healing samples with powder additives were also higher. The maximum difference in air content which was +2.6% over the control sample was exhibited by Fp_B. Fly ash had the highest absorption rate of the coating liquid among the powder type additives (see Table 4.2) thereby the amount of the of coating liquid contained in Fp_B was the highest among the self-healing samples. This is likely the reason for the uppermost air content exhibited by this sample. The presence of this coating liquid is expected to increase the fluid content with in the mix. As the fluid content increases, more free water is expected to be available for the generation of air bubbles, so air content likely increases.

The zero drop flow values for the mortar with powder type additives are measured immediately after casting following the JIS R 5201 guidelines and the results are shown in Table 4.4. The experimental results show that similar to the case of air content Fp_B sample containing 120 kg/m3 of Fly Ash resulted in the higher flow likely due to the higher amount of coating liquid used to saturate the material.

4.4.2 Compressive strength of mortar mixes with PCA and powder type additives

Fig. 4.19 compares the compressive strength of the self-healing mortar specimen at the age of 7th and 28th day after casting. The specimen were kept in sealed curing condition at a temperature of 20 ^{0}C until the compressive strength test was conducted. Depending on the material composition and compact formation pressure and the dosage of PCA, the differences in self-healing mortar strength varied from 5 MPa fall (PC2_1B) to 18 MPa rise (PC4_2A) at 28 days compared to the control mix type.

Considering the material composition, addition of the 3rd group of PCA with OPC content of 70% by mass resulted in higher mortar compressive strength at 28 days compared the 1st and 2nd group of PCA. PCA formed with 25 MPa formation pressure resulted in slightly higher compressive strength mortar than those formed with 10 MPa with the same material composition. The highest compressive strength was observed for mortar made with group 4 PCA, with 50% sludge content by weight, probably due to the strength improvement of the compacts by sludge as pointed out by Sakai et al. (2015) [44].

Thus, it may be concluded that the addition of PCA as partial sand replacement brings about a difference on the compressive strength depending on the constituent materials. However, the long term effect of PCA saturated with coating liquid still needs to be investigated beyond 28 days of age.

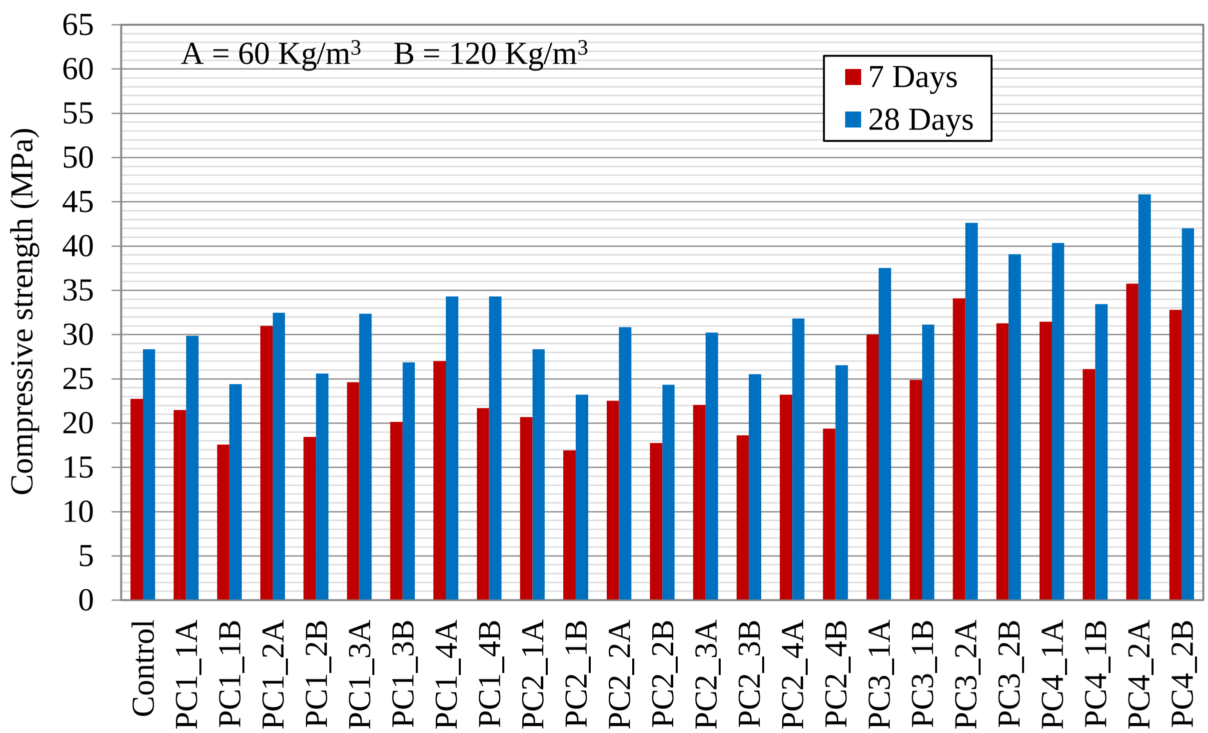


Figure 4.19 Compressive strength of mortar with PCA type of additives

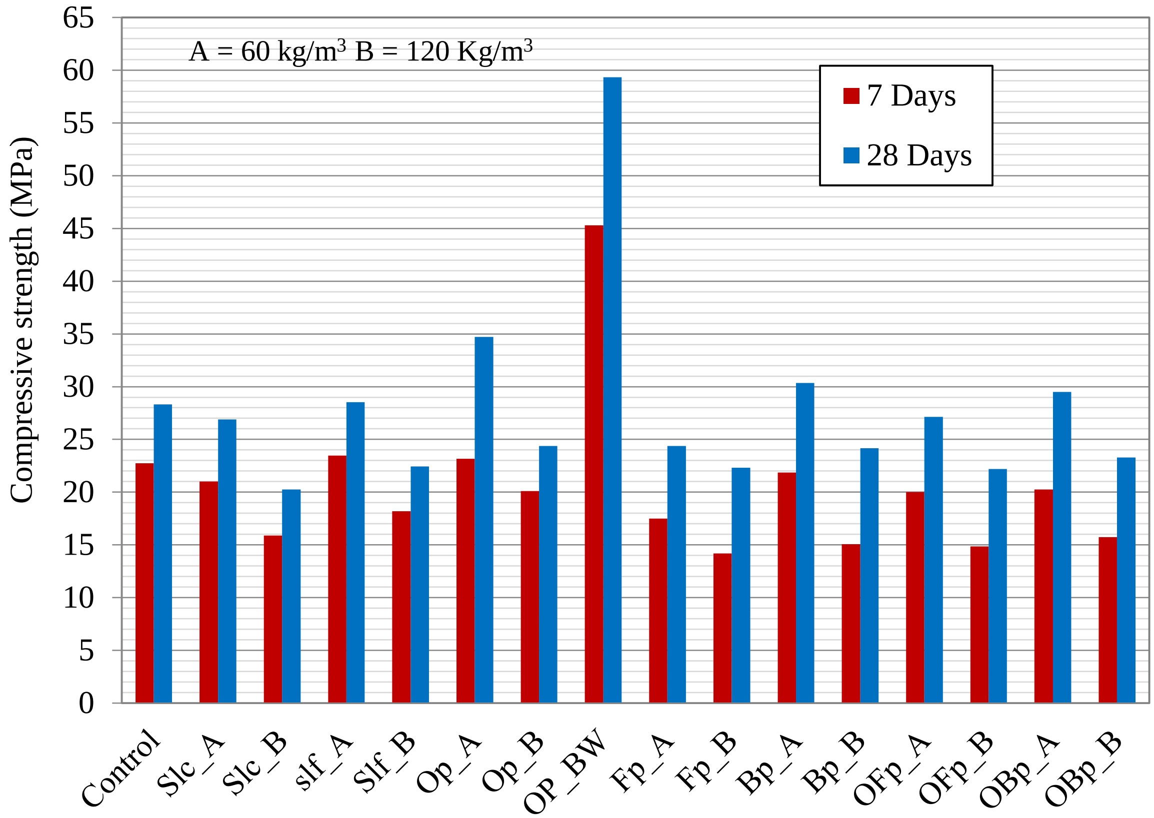


Figure 4.20 Compressive strength of mortar with powder type of additives

The compressive strength of the powder type self-healing additives after 7 and 28 days of casting are presented in Fig. 4.20. According to the results OP_BW which contains 120Kg/m_3 of OPC without coating liquid as sand replacement showed the highest strength among the group. The Op_B sample which contains 120 kg/m3 of OPC saturated by coating liquid (see Table 4.2 for coating liquid absorption rate) on the other hand had half the strength of Op_BW st the end of 28 days. This indicates that the addition of coating liquid helps to reserve the hydration potential of the added self-healing materials and protect the powders from contact with water during mixing.

Considering the material type, at the age of 28 days the samples with pozzolanic powders showed similar strength range compared to the with Op_A and Op_B incorporating coating liquid saturated OPC as self-healing additives. Nevertheless, beyond 28 days pozzolanic action is expected to bring in higher strength values for the samples compared to those containing OPC.

4.5 Water pass test results of PCA and powder type additives

Fig. 4.21 - 4.24 present the water pass test results of for 28 days old mortar specimen. It can be seen from the results that all specimen showed rapid reduction in the measured flow for up to the 7th day and the value stabilized for the following period. At the end of the 14th day water pass test, secondary vacuum soaking was conducted to exclude the effect of invisible micro and nano bubbles that could be entrapped in the crack space causing pseudo flow reduction [37, 38]. This secondary vacuuming removes entrapped air bubbles inside the crack hence sudden rise in the measured water flow by removing pseudo flow reduction effect. The procedures of the second stage vacuuming are listed in section 3.2.1.

Comparison of the water flow reduction at the 14th day (see Fig. 4.27) was calculated by equation 4.1 to confirm the self-healing ability of mortar excluding air bubble effect in comparison with control mortar without PCA.

$$Flow\ reduction = \left(\frac{f0-f14}{f0}\right)\ x\ 100 \ \ldots\ldots \text{(Eqn. 4.1)}$$

Where,

f_0 : average flow at day 0

f14 : average flow at day 14

Before vacuuming, all samples seemed to have high water flow reduction at 14th day of the water pass test. But after vacuuming it was revealed that compared to the control sample, self-healing mortar samples incorporating PCA showed a good tendency to have better water flow reduction at the 14th day of the test for the considered crack width, 0.3 mm compared to the control sample. The experimental results revealed that at this stage higher dosage (120 kg/m3) of the PCA type self-healing additives was required to show better water flow reduction after vacuuming. Among the PCA group, the peak water flow reductions for mortar (48% and 40%) were achieved by PC1_1B & PC2_2B respectively which contain fly ash (Fig. 4.27).

Nevertheless, the observed water flow reduction values are not considered to be fully satisfactory given the test was conducted using young age specimen of 28 days old. Therefore, further study is recommended to improve the performance of PCA taking into consideration the material composition, their particle size and formation pressure.

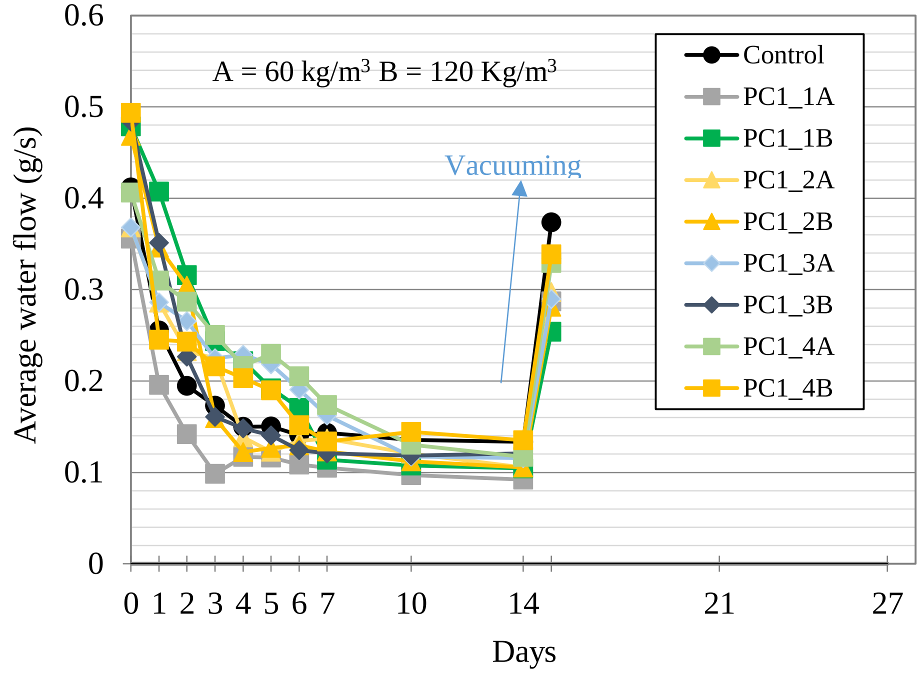


Figure 4.21 Water pass test result for mortar with group 1 PCA

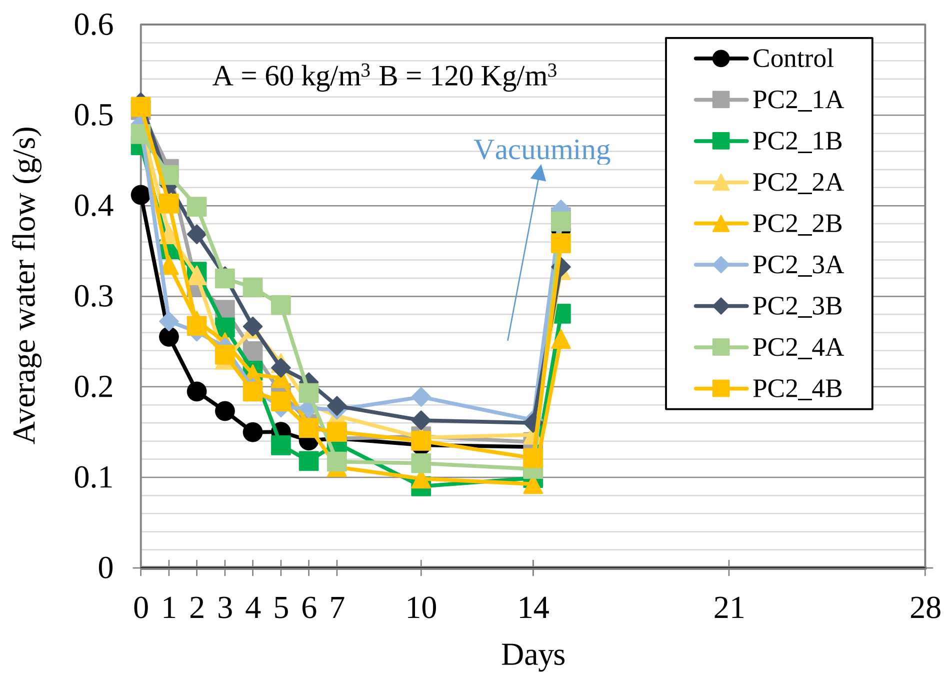


Figure 4.22 Water pass test result for mortar with group 2 PCA

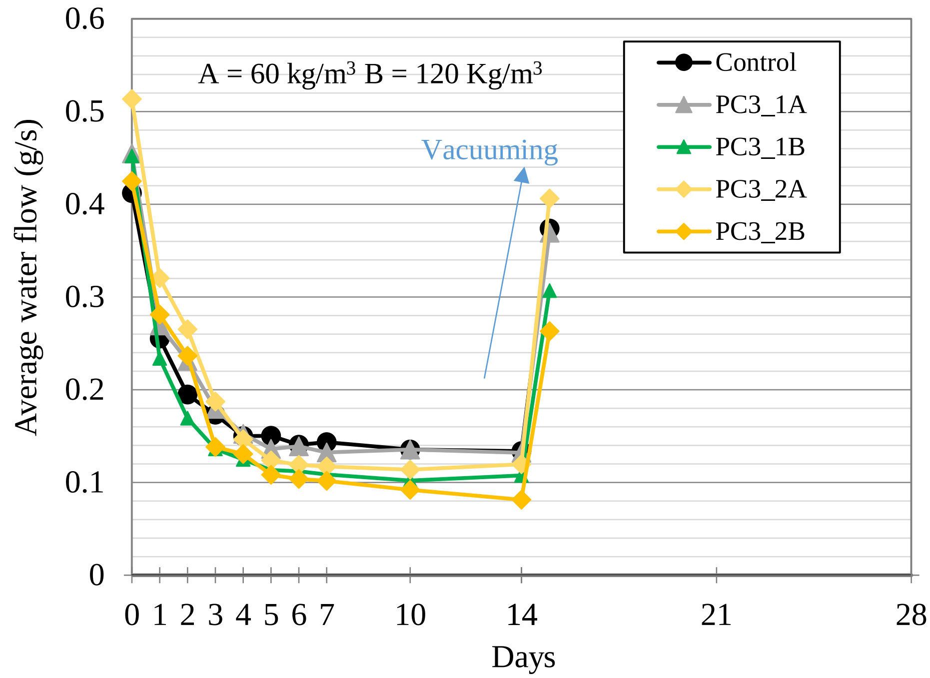


Figure 4.23 Water pass test result for mortar with group 3 PCA

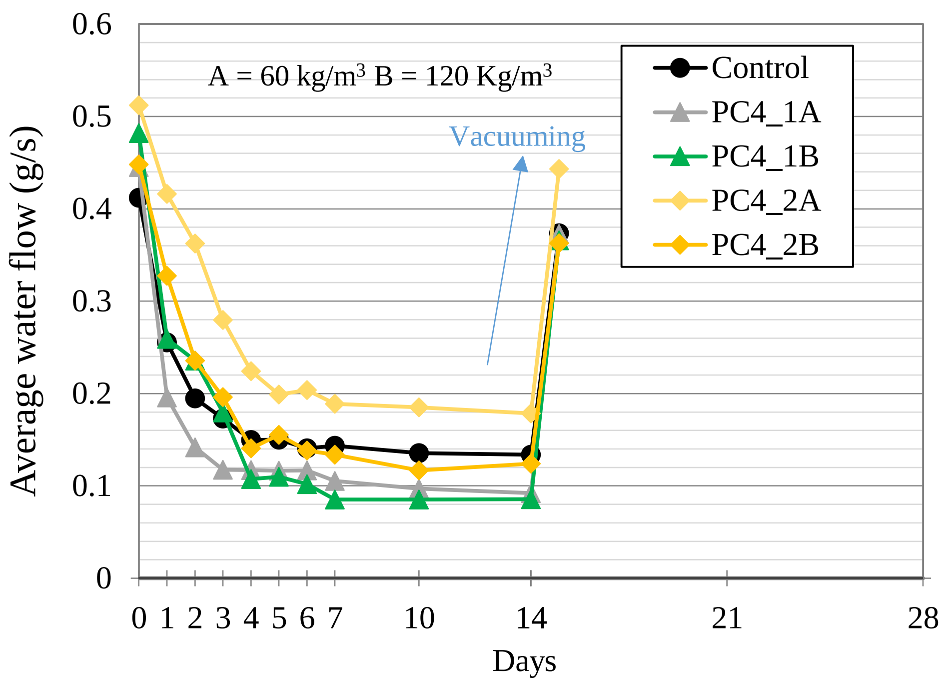


Figure 4.24 Water pass test result for mortar with group 4 PCA

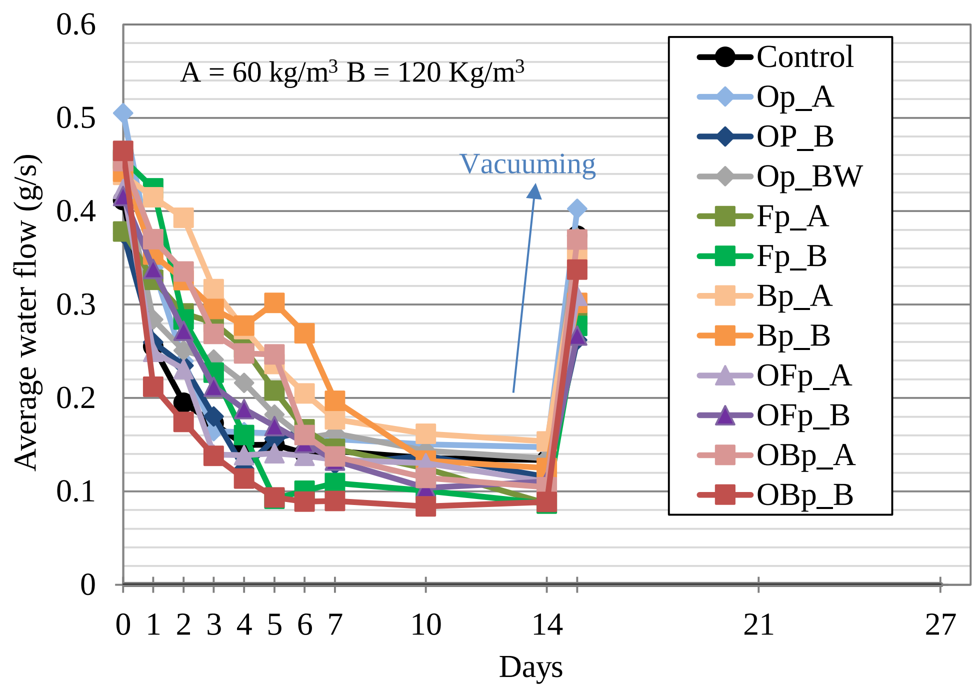


Figure 4.25 Water pass test result for mortar with group 4 PCA

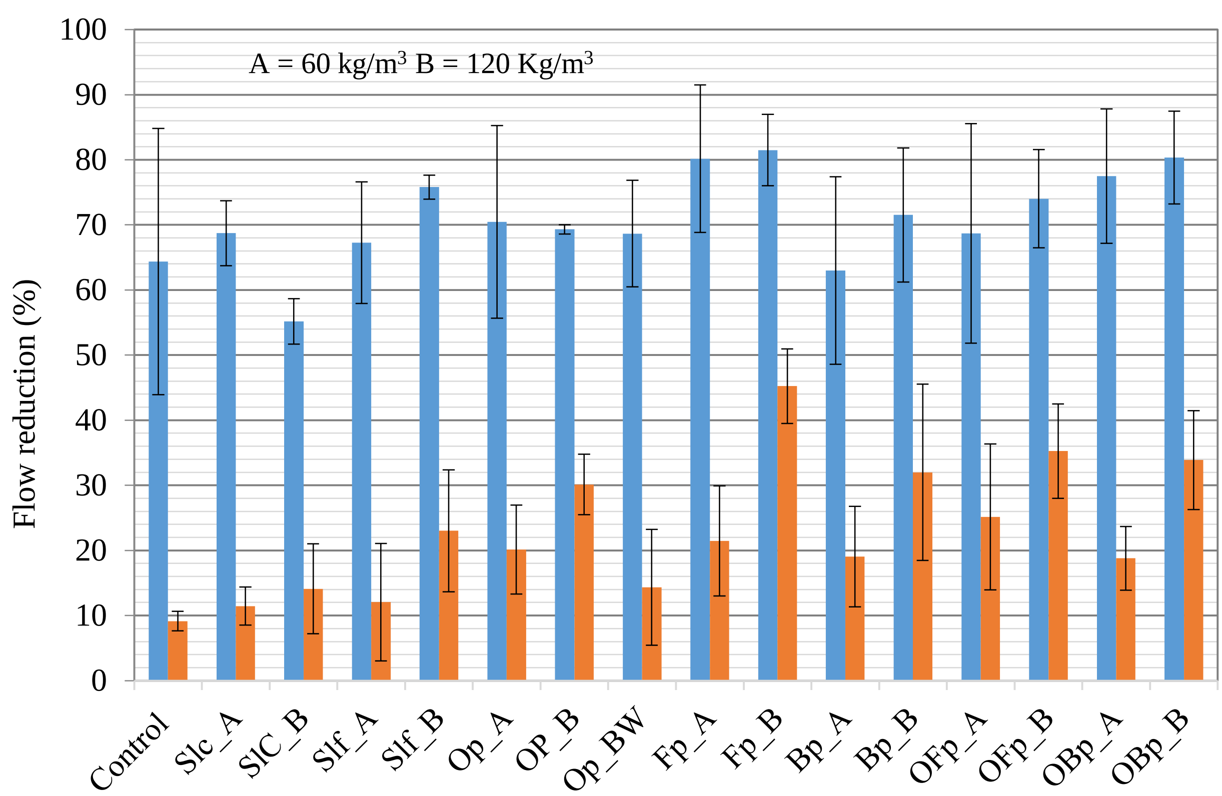


Figure 4.26 Water flow reduction at the 14th day for mortar with powder type additives

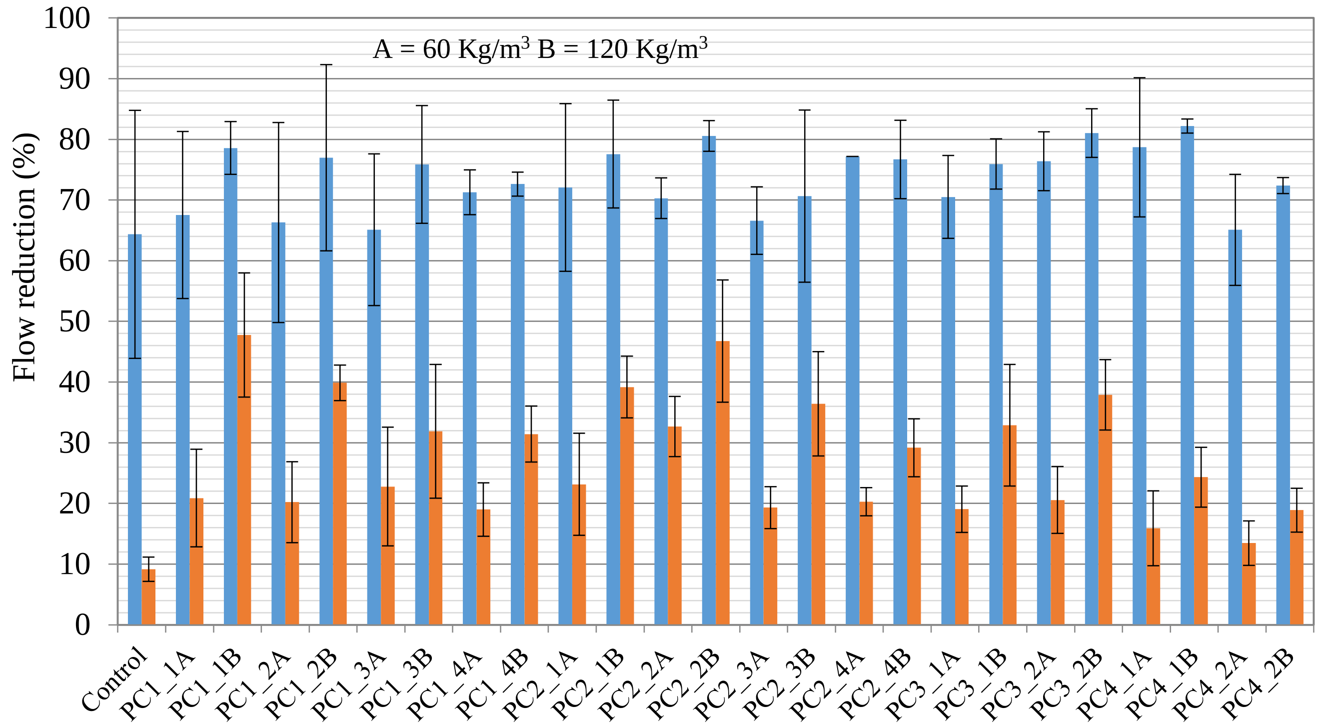


Figure 4.27 Water flow reduction at the 14^{th} day for mortar with PCA type additives

Inclusion of expansive agents and geo materials capable of expanding and swelling up on contact with water as recommended by previous studies [4, 33] could therefore be one possible way to improve PCA performance. Substantial improvement in self-healing technology could be achieved by powder compaction technology improving the set-backs of granulation technique. This methodology is also beneficial for creating sustainable environment also as it helps to re-use of sludge, a factory waste product.

Fig. 4.25 presents the average flow measurements in gm/s for 28 days old specimen at average crack width provision of 0.3 mm for mortar made with powder type self-healing additives. The results show that initial flow values for all samples exhibited rapid drop for up to the first 7 days after the start of water pass test. After the 7^{th} day this flow rate is observed to have gradual reduction up until the 14^{th} day water flow measurements (see Fig 4.25).

At the end of the 14^{th} day secondary stage vacuuming was conducted according to the procedures described in section 3.2.1. This step resulted in revival of the water flow values. The observed increase in water flow measurement is likely due to the removal of the entrapped air bubbles inside the crack gap during water flow measurements.

So as to compare the self-healing ability of each sample, the 0^{th} day initial water flow values are compared with their respective values at the end of the 14^{th} and 28^{th} day of the water flow measurements. This comparison is done both for before after conducting vacuuming for each of the samples. Fig. 4.26 summarizes the water flow reduction in % for 28 days old mortar specimen at average crack width provision of 0.3 mm at the 14^{th} day of water pass test of water pass test. The presented values in percentage are the results of averaged flow reduction values for three specimen for each sample.

Figure 4.26 reveals that at the values of the average water flow reduction at the end of 14 days of water pass test before vacuuming was 64 %. While after vacuuming the value plummeted to 9 %. Inclusion of coating liquid saturated coarse sludge powder showed no major improvement over the control sample after vacuuming. At a dosage rate of 120Kg/m^3, however, incorporation of fine sludge to the sample improved the water flow reduction to approximately 23%. After vacuuming it can be clearly seen that the highest flow reduction of 45% was achieved by Fp_B, the sample incorporating coating liquid saturated FA at 120 kg/m^3 of mortar.

Comparing Fig. 4.26 and 4.27, it can be said that the maximum water flow reduction achieved by the PCA type of additives (48%) is still within the range of water flow reduction values achieved by adding powder type cementitious materials (maximum of 45%). At this stage no major improvement was not seen by additional compaction and inclusion of PCA over the powder type approach.

4.6 Challenges of utilizing PCA as self-healing additives

Powder Compacted Aggregate (PCA) are manufactured by compacting mixture of sludge powder and cementitious materials and re-crushing the formed compacted material. The sludge which is used to bind the cementitious materials is a byproduct of concrete manufacturing plants (filtered washout of truck mixers) and thus not a costly material. On the other hand, sludge powder is produced after drying the sludge cake and finely grinding it to a size of 105 μm or less and its preparation is considered as an energy consuming process. Additionally, after compaction of the combined prepared sludge powder and cementitious materials, the compacts have to be crushed to a pass sieve size of 1.18 mm. The expected high energy consumption of manufacturing PCA type of additives is not considered a challenge in itself had the self-healing of the mortar samples made with PCA was better than those with powder type of additives.

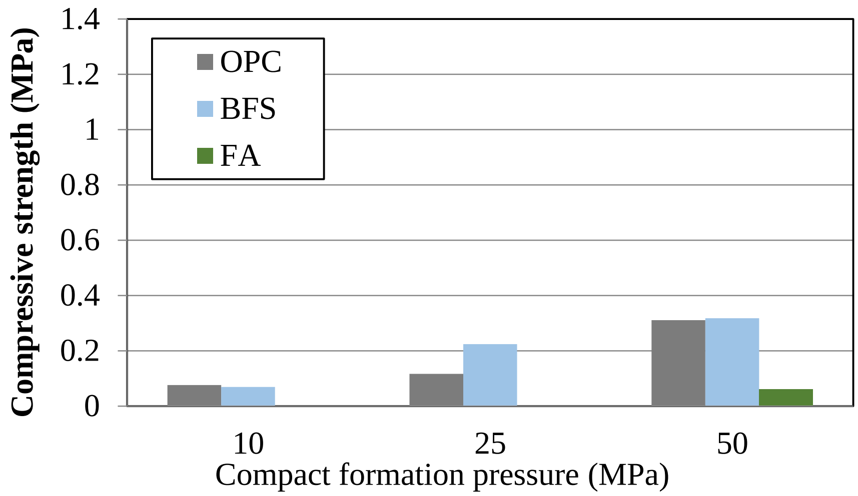


Figure 4.28 Compressive strength of compacts of OPC, FA & BFS

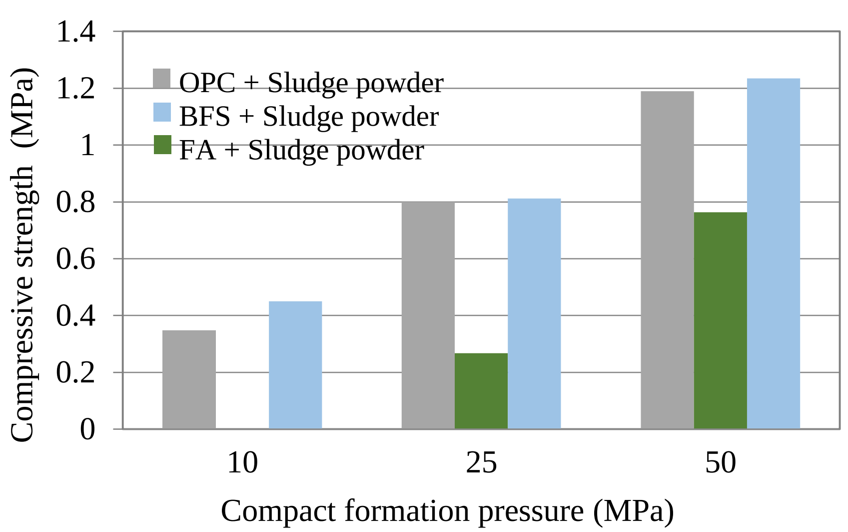


Figure 4.29 Compressive strength of compacts of sludge and OPC, FA & BFS mixtures

The compressive strength of the powder compacts resulting from the cementitious materials in their pure form and the respective formation pressure is presented in Fig. 4.28. For the applied pressure ranges of 10 – 50 MPa with duration of 1 minute, the resulting compacts had very low strength (less than 0.3 MPa). Addition of sludge powder to the cementitious materials at a ratio of 1:1 brought about a major strength improvement as can be seen in Fig 4.29. Yet, the PCA which were manufactured with formation pressure of 10 and 25 MPa still have low strength less than 0.8 MPa. And this strength range they could not likely survive the mixing process; hence could not show any better performance over the powder type additives.

4.7 Chapter summary

Previous studies conducted on recycling concrete by powder compaction by Sakai et al. (2015) have revealed that it is possible to form solid compacts of cementitious materials by combining them with dry sludge powder. In this method, the use of water to make granules would not be required since the sludge powder could serve as a dry binding agent for the self- healing powders during compaction. In this study, powder compacted aggregates (PCA) made from sludge and ordinary Portland cement, blast furnace slag and fly ash were introduced as self-healing additives partially replacing sand.

The PCA were prepared by compacting the powder mixtures inside a cylindrical mold using universal testing machine and crushing the resulting compacts by jaw crusher. After conducting water pass tests, it was shown that inclusion of the PCA contributes to water flow reduction. However, the performance of the samples incorporating PCA was not found out to be satisfactory given relatively young specimen of age 28 days were used for the experimental study. In addition, at the chosen formation pressures for the compacts the strength of the compacts themselves was very weak for the PCA to survive the mixing process of the mortar. Hence, the performance of the PCA could not be any advantageous over powder type self-healing additives (binary mixtures) with similar material compositions. Further research is needed to improve water flow reduction of the self-healing mortar by selecting ingredients of the PCA as well as optimizing the formation pressure and size distribution of PCA.

Ikoma et al. (2014) has revealed that the initial high rate of flow reduction in water past test results is attributed to the generation of air bubbles with in the crack gap of concrete. Kayondo & Kishi (2016) pointed out that the formation of large air bubbles on crack surfaces will not occur when less than 100% air saturated water was used for water pass tests. Therefore, equilibrated water having an average DO content less than 95 % was utilized for conducting all water pass tests in this study to avoid the influence of large air bubbles on the water flow measurements. At the end of the 14th days of the water pass test, secondary vacuum soaking was introduced to exclude effect of invisible air bubbles on the measured water flow and to verify the flow reduction resulting from solid precipitation and deposition only. Initially all the samples exhibited high water flow reduction, after the second stage vacuuming it was revealed that samples with PCA and powder type additives show better flow reduction compared to the control.

CHAPTER 5 PARTIALLY HYDRATED CEMENT GRANULES AS CRACK SELF-HEALING ADDITIVES

5.1 The use of coating liquid and its hydration reaction retarding effect - Background

Meta (2018) investigated the possibility of using heated sludge powder saturated with a coating liquid as a self-healing additive that partially substitutes sand. According to the study, sludge powder could recover its reactivity by heating it up 400 °C. Moreover, the coating liquid was shown to have a reaction retarding effect which could keep the reactive sludge and unhydratred cement particles from reaction for long time. Fig. 5.1 presents the calorimeter test results of 100% OPC paste, and those containing fine sludge powder saturated with coating liquid from 5 - 20 % by weight. According to the results, cement paste samples which contained the saturated sludge powder exhibited lower heat of hydration reaction and achieved their peak hydration rate slightly later than the OPC paste (see Fig. 5.1). Based on these results, this type of coating liquid is considered to have promising hydration reaction retarding effect, which could make it useful to come up with self-healing concrete designs with use cement hydration as main self-healing mechanism [46].

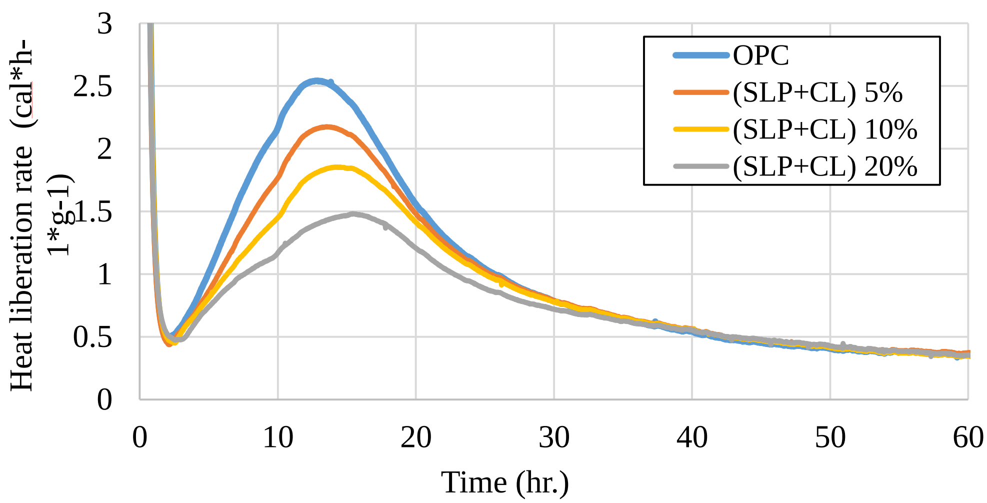


Figure 5.1 Calorie meter test results for OPC paste and OPC paste with coating liquid and sludge powder [46]

However, at higher dosages the coating liquid was found out to disrupt the compressive strength development. Fig. 5.2 illustrates the compressive strength of mortar samples in which the sand was replaced by heated sludge and coating liquid saturated heated sludge from 5 - 20% by weight of sand. Introduction of heated sludge powder to mortar mixes caused no major change in the compressive strength at 5 and 10% sand replacement; however, same dosages of coating liquid saturated sludge caused about 15 and 25 MPa strength reduction respectively. 20 % saturated sludge replacement of the sand resulted in the lowest compressive strength among the group, having compressive strength less than 10 MPa (see Fig. 5.2). Accordingly, the strength reduction is attributed to the presence of the coating liquid and not to the presence of sludge powder.

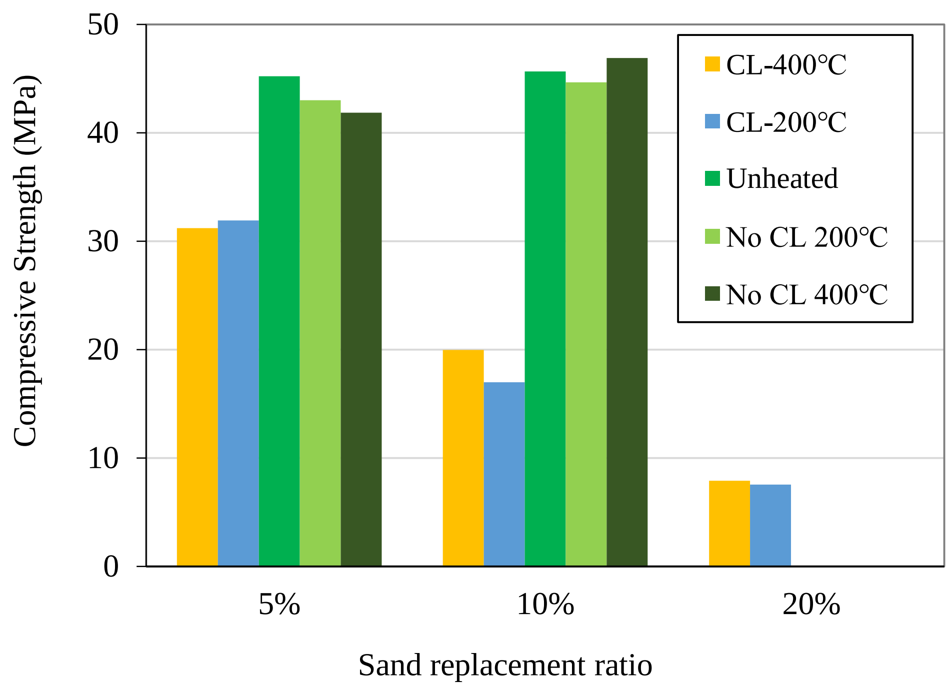


Figure 5.2 Compressive strength of 28 days old mortar specimen [46]

Three months old mortar specimen for which their strength is presented at 28 days in Fig. 5.2 exhibited only an average of 13.43 MPa indicating the retarding of hydration reaction by the coating liquid for the test duration. These samples of mortar which contain a significant amount of unhydratred cement were crushed to pass 4.75 mm sieve and mixed with cement and water to give self-healing mortar (M) with w/c of 0.5 for which the water pass test results are compared with control specimen of same w/c and cement to sand ratio of 0.4 (see Fig 5.3).

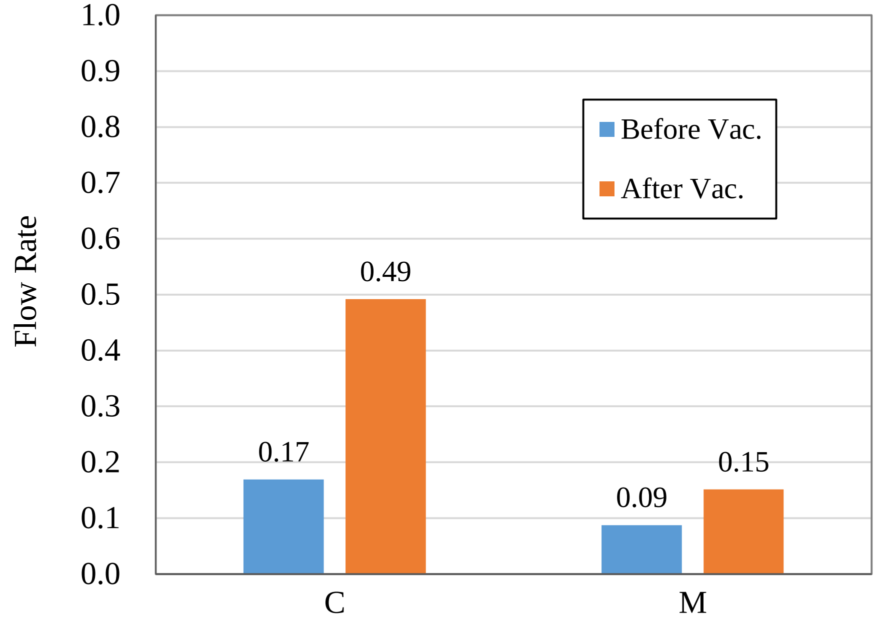


Figure 5.3 Water flow rate results at 28th day of water pass tests for control (C) and self-healing mortar (M) samples [46]

Fig. 5.3 illustrates the water flow rates for the control and self-healing mortar before and after vacuuming at 28 days. According to this result, it was possible to confirm that for the case of control specimen flow rate grew up to about 50% while in case of the self-healing samples the average flow rate revived to only 15%, indicating a good sign of crack closing and self-healing ability of the M type of samples.

The crack surfaces observations of the samples by microscope at the end of the water pass test are shown in Fig 5.5. It can be clearly seen that the formed products inside the crack are different for the two cases where the crystals are comparatively larger in size for the self-healing case. In addition, bottom crack surface observation of the two types of samples exhibited a difference in the amount of products formed closing the crack gaps [46].

These observations are thought to lead to the new way of using the coating liquid to enhance self-healing ability of concrete. The unreacted cement particles inside the crushed mortar that was used to make the M type of specimen were expected to contribute to more hydration product formation during the water pass tests duration.

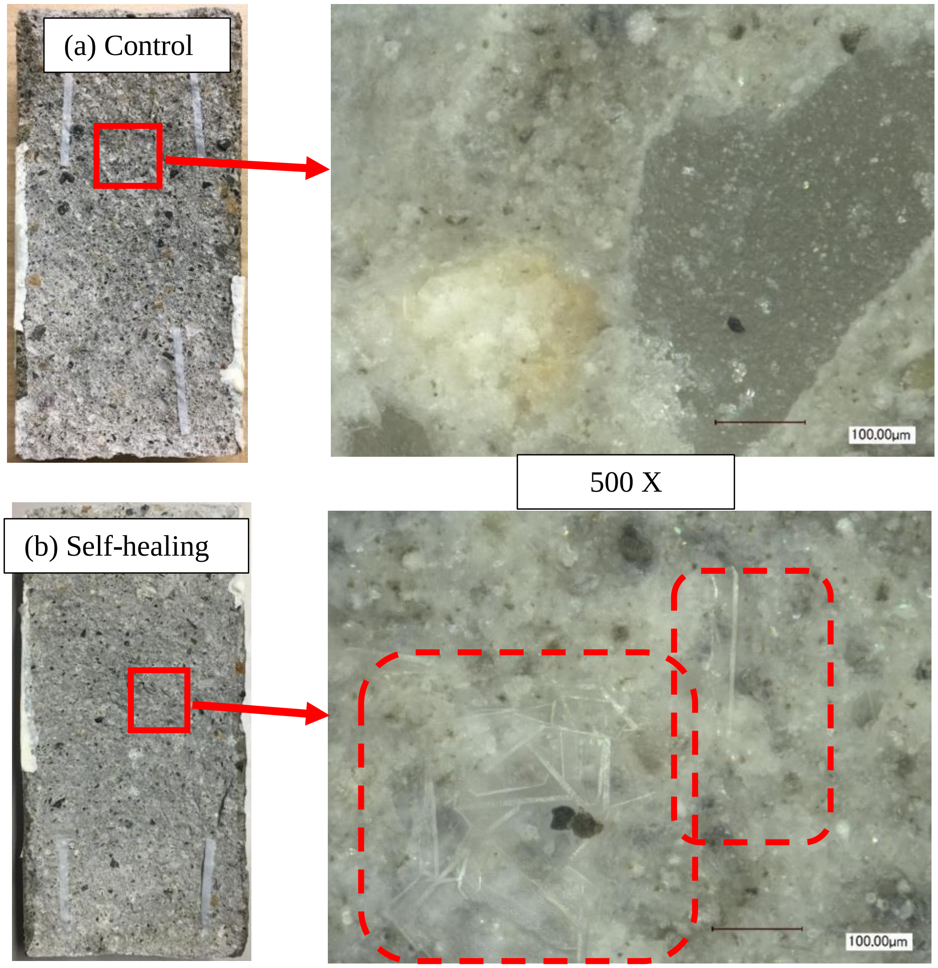


Figure 5.4 Microscopic observations of control mortar (a) and self-healing mortar /M/ (b)

5.2 Preparation of partially hydrated cement granules

5.2.1 Materials

(1) Ordinary Portland cement

Type I Japan Portland cement with density of 3.15 g/cm^3 was used.

(2) Silica fume (SF)

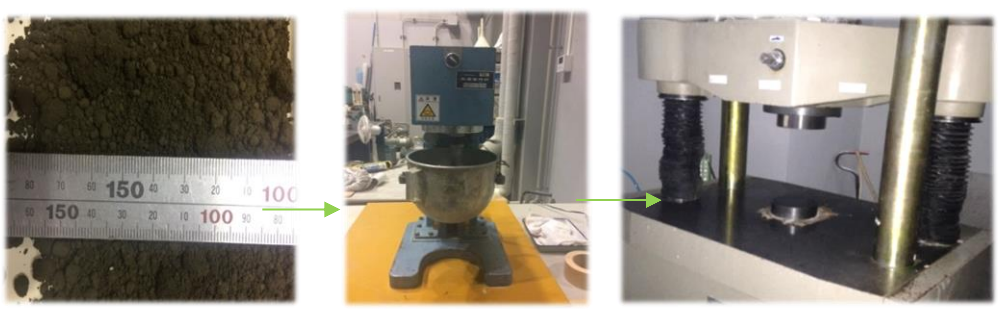
JIS A 6207:2008 silica fume fine powder for concrete having density of 2.09 g/cm^3 and specific surface area of 20 m^2/g was used.

(3) Coating liquid (CL)

In this research, Polyethylene Glycol 400 (PEG 400) was used as coating liquid (CL) to protect cement particles from reaction during mixing and to temporarily preserve them until they become in contact with water when crack opens at later matured stages. PEG 400 is a low-molecular-weight grade of polyethylene glycol. It is a clear, colorless, viscous liquid that is widely used in a variety of pharmaceutical formulations. PEG 400 is soluble in water, acetone, alcohols, benzene, glycerin, glycols, and aromatic hydrocarbons, and is slightly soluble in aliphatic hydrocarbons.

5.2.2 Procedures and trials leading to granule preparation

Preliminary tests were conducted with the aim of understanding the relationship between the amount of coating liquid in cement paste mixtures and the compressive strength development as indicator of the hydration degree of cement particles. These preliminary tests are the basis upon which weak self-healing granular additives can be designed with reserved hydration potential using coating liquid. Initially, OPC is hand mixed with the coating liquid with cement to coating liquid ratios ranging from 7 to 20% by mass of OPC. Next the coated OPC is mixed with water making cement paste in a mortar mixer for 3 minutes. The w/c of the cement paste in this range was set to 0.15 and 0.20 to minimize the cement hydration as much as possible. Lastly, the produced pastes are tested for compressive strength at 7 days and 28 days after casting. Fig 5.5 briefly summarizes the procedures of the preliminary tests.



(a) (b) (C)

Figure 5.5 Summary of preliminary test procedures: (a) mixing OPC and CL (b) cement paste mixing using mortar mixer (C) testing compressive strength by universal testing machine

Figure 5.6 presents the relationship between the coating liquid to cement ratio and compressive strength of 7 days and 28 days old cement paste having w/c of 0.2 and 0.15. At 0.20 w/c, the compressive strength was the highest at 7% coating liquid to cement ratio and its value declined with the increment of the coating liquid content. This result is natural and expected as the coating liquid has been shown to disrupt strength development at higher dosages. When the w/c is reduced to 0.15, however, very dry harsh mixes (see Fig. 5.7) were formed for coating liquid/cement ratio of 7 and 10%. These type of very dry intermediate products resulting for 0.15 w/c are taken as indications for ranges of water to cement ratios and coating liquid contents to result in granular self-healing additive that contain unhydratred cement inside. Accordingly it is decided that the total liquid (water + coating liquid)/cement range should be less than or equal to 0.25 to result in granular type of products. As the coating liquid/cement ratio increased to 15 and 20 % pastes with very small strengths, less than 10 MPa at 28 days, could be formed.

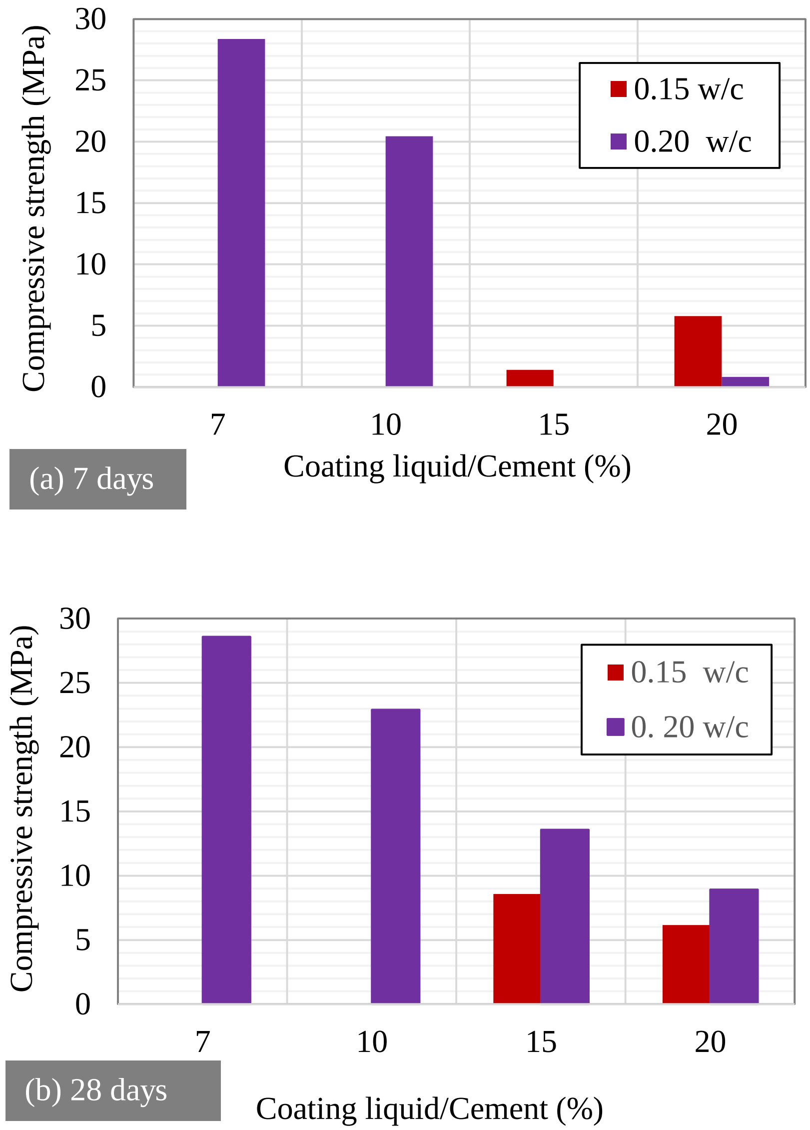


Figure 5.6 The relationship between coating liquid/cement & compressive strength of OPC paste: (a) 7 days old samples (b) 28 days old samples of preliminary trials

(a) (b)

Figure 5.7 Intermediate (dry) products formed for 0.15 w/c (a) Coating liquid /C = 7%, (b) Coating liquid /C = 10%

The coating liquid/ total liquid ratio is another important parameter for the design of the granular additives and its relationship between with the compressive strength of the cement pastes is shown in Fig. 5.8. It can be observed that for the considered w/c of 0.2 and 0.15 ranges less than 0.35 resulted in compressive strength of 20 MPa and higher. This level of compressive strength is considered a very high value, hence high amount of hydrated particles. Therefore the ranges 0.35 to 0.55 are selected for the coating liquid to total liquid ratios to have reserved unreacted cement particles as much as possible.

Based on these preliminary test results, different trials are conducted to design and manufacture very fine and not so strong cement granules as self-healing additives that can substitute sand. Two types of granules were prepared based on the material composition. Type I trials consisted of OPC as main hydrating component only while Type II trials contained OPC and SF. Table 5.1 and Table 5.2 summarize the mix compositions and size of the trials leading to the final granules with reserved hydration capacity. For case I the total liquid to powder (cement) is varied from 0.3 to 0.15 while for case two the ratio was varied from 0.225 to 0.15. The addition of SF to the type II granules is done so as to reduce the amount of water needed for manufacturing them since the very fine SF particles can act as filler of the space between the cement particles.

The mixing procedure was as follows for Type I and Type II trials. For Type I cases the mixture of liquids was prepared by mixing the coating liquid and water in different desired ratios. After that OPC and the liquid mixture are mixed in mortar mixer at medium speed for 1 minute followed by 3 minutes of high speed mixing. For Type II trials the mixture of coating liquid and water is similarly added to OPC and mixed in mortar mixer for 1 minute at medium speed after that SF is added at a ratio of 10 % of the weight of OPC and mixing is done 3 minutes at high speed. The high speed mixing is then continued for additional 7 minutes until the SF is well incorporated to the mix. The total mixing time for the Type II cases is, thus, 11 minutes.

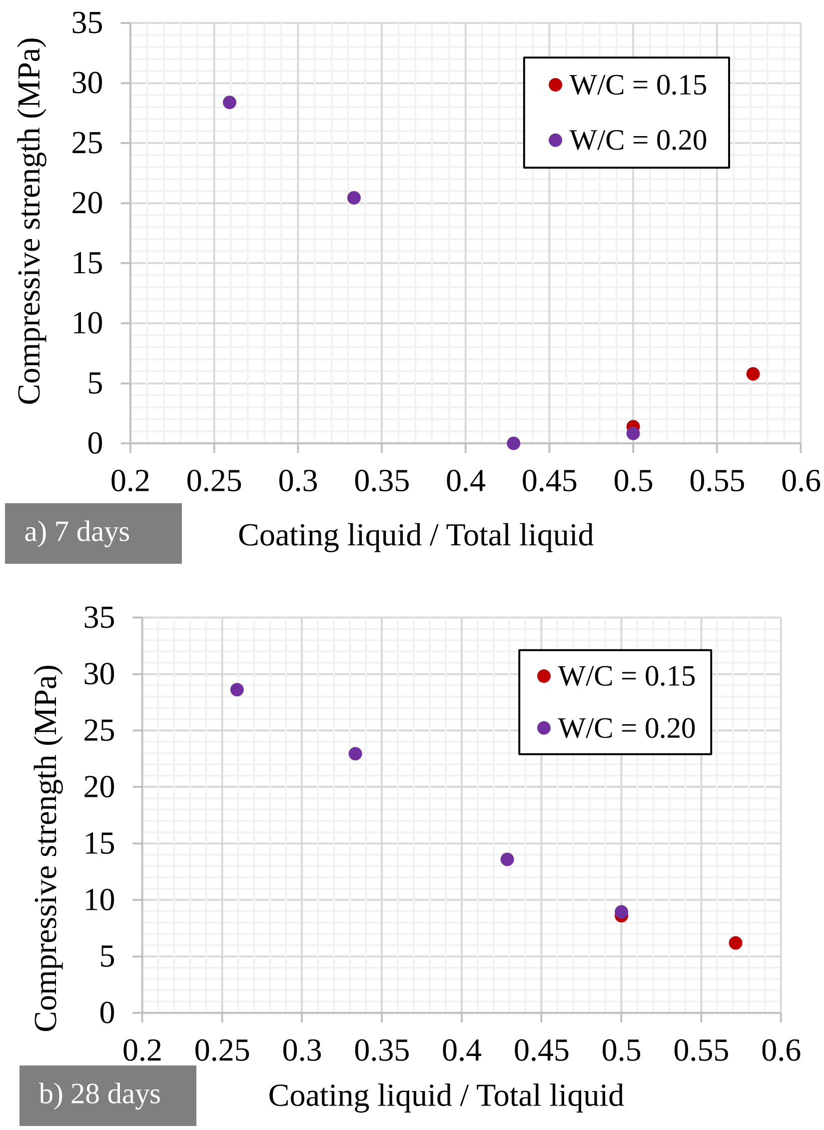


Figure 5.8 The relationship between coating liquid/total liquid and compressive strength of OPC paste: (a) 7 days old samples (b) 28 days old samples of preliminary trials

Table 5.1 Summary of trials leading to Type I: OPC granules with reserved hydration capacity

No.	Total liquid/ Cement	Coating liquid/ Total liquid	Flow (mm)	Notes	Pictures
1		0.35	87.4		
2		0.4	87.2	Paste with Plasticine clay type texture	
3	0.30	0.45	87.1		
4		0.5	87.1		
5		0.55	87		
6		0.35			
7		0.4			
8	0.25	0.45	..	Dry mix	
9		0.5			
10		0.55			
11		0.35			
12		0.4		Dry mix	
13	0.225	0.45	-		
14		0.5		(1-2 cm size)	
15		0.55			
16		0.35			
17		0.4			
18	0.20	0.45		Granules (< 5mm)	
19		0.5			
20		0.55			
21		0.35			
22		0.4			
23	0.175	0.45		Granules (<2 mm)	
24		0.5			
25		0.55			
26		0.35			
27		0.4			
28	0.15	0.45		Granules (<1 mm)	
29		0.5			
30		0.55			

Table 5.2 Summary of trials for Type II: OPC + SF granules with reserved hydration capacity

No.	Total liquid/ Cement	Coating liquid/ Total liquid	Flow (mm)	Notes	Pictures
1	0.25	0.35	-	Sticky consistency: can be cast with vibrator	
2		0.4			
3		0.45			
4		0.5			
5		0.55			
6	0.20	0.35	..	Dry mix (1-2 cm)	
7		0.4			
8		0.45			
9		0.5			
10		0.55			
11	0.175	0.35	-	Granules (< 3 mm)	
12		0.4			
13		0.45			
14		0.5			
15		0.55			
16	0.15	0.35		Granules (< 1 mm)	
17		0.4			
18		0.45			
19		0.5			
20		0.55			

For each ratio of total liquid to powder the coating liquid to total liquid is varied as 0.35, 0.40, 0.45, 0.50 and 0.55. This is done so as to consider the effect of the coating liquid to total liquid ratio on the maximum sizes of the manufactured granules. However, it was found out that the size variation was mainly dependent on the former ratio: total liquid to powder ratio. The size variations along with total liquid to powder ratio of the trials are summarized in Table 5.1 and Table 5.2.

5.2.3 Criteria for selecting granules from the trials

A total of 15 granules were prepared for type I case while for type II case 10 granule types were manufactured varying based on their total liquid to powder ratios and the proportions of the coating liquid and water (See Table 5.1 and 5.2). The granules are listed as numbers 15-30 for Type I and from 11-20 for Type II cases. As basic study parameter it was found important to decide the coating liquid to powder ratio to a single value. This parameter affects the hydration degree there by the mechanical strength of the pastes and granules formed. For that reason compressive strength is chosen as an indicator of the reservation of hydration capacity within the granules; the higher the compressive strength the lower the remaining hydration potential and vice versa.

Fig. 5.9 shows the relationship between coating liquid/total liquid and compressive strength of the cement pastes which are the first five series presented in Table 5.1 and Table 5.2. The Type 1 case has total liquid to powder (Total liquid / cement ratio) of 0.3 while Type II case has total liquid to powder (Total liquid/ (OPC + SF) of 0.25. This ratios are selected as the minimum ratios needed to make cement paste which can be cast in to molds there by tested for its compressive strength. Even though, these compressive strength values may not be exactly the same as the strength of the granules themselves, the values are expected to approximate the strength or the hydration degree of the granules to an acceptable limit.

According to the results, at the age of 7 days the measured compressive strength of all cement pastes (both OPC and OPC+SF case) were less than 5 MPa for coating liquid to total liquid ratios of 0.4 and more. However, compressive strength development continued for all samples and at age of 28 days samples with coating liquid/total liquid 0.45 and less exhibited compressive strength of 15 MPa and greater. For the purpose of reserving the hydration potential inside the granules as much as possible the proportion of the coating liquid to total liquid is therefore decided to be 0.5 as the cement paste samples at this ratio had showed small strengths of 9 MPa for OPC paste and 6 MPa for OPC + SF case respectively (see Fig 5.9). The range of compressive strength value less than 10 MPa is taken as good indicator of potential reservation of cement hydration that can contribute to self-healing as in the study conducted by Meta (2018), the recycled mortar which were used to replace sand in self-healing mortar had similar strength values, approximately 8 MPa, at the age of 28 days (see Fig 5.2). The selected granules for self-healing mortar preparation are therefore summarized in Table 5.3 below.

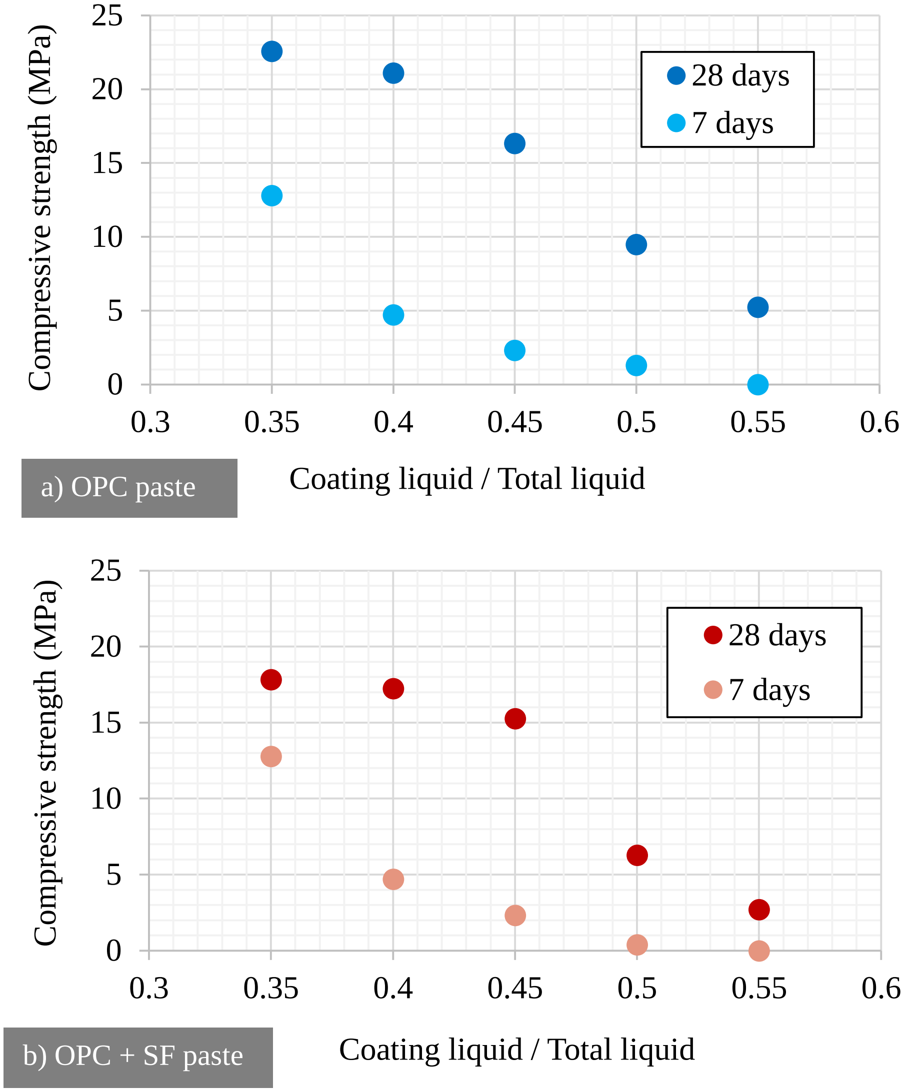


Figure 5.9 The relationship between coating liquid/total liquid and compressive strength of cement paste: (a) Type I: total liquid /cement = 0.3 (b) Type II: Total liquid/powder =0.25

Table 5.3 The mix proportions of granules selected for the self-healing mortar preparation

Name	Total liquid/ Powder	Coating liquid/ Total liquid	Silica fume/powder	Notes on powder type
I-0.2	0.2	0.5	0	**OPC case: Type I**
I-0.175	0.175		0	
I-0.15	0.15		0	
II-0.175	0.175		0.1	**OPC + SF case: Type II**
II-0.15	0.15		0.1	

5.3 Effect of granules on fresh and hardened properties of mortar

Fig. 5.10 presents the results of the air content for the mortar mixes right after casting is done according to the guidelines of JIS A 1128, method of test for fresh concrete by pressure method. The experimental results revealed that the maximum air content difference of 2% increase belonged to the I_0.175 granules at granule dosage rate of 60 as well as 120 Kg/m3. The mortar containing type II granules (OPC+SF case) exhibited very small air content difference with the control. The sample containing II_0.175 granules exhibited a maximum air content increment of only 1 % approximately over the control while for cases with II_0.15 granule the air content values show decrease by about 0.5% at granule dosage rate of 120 Kg/m^3 of mortar.

Most concrete mix design guidelines allow a variation of ± 1 % from the target air content of concrete mixes. According to the results for the mortar samples with Type I granules which showed a maximum difference of +2 % from the control could be considered as mild effect that needs to be addressed during the initial mix design stage. The effect of the Type II granules on the air content, however, is within the acceptable limit of ± 1 % difference compared to the target.

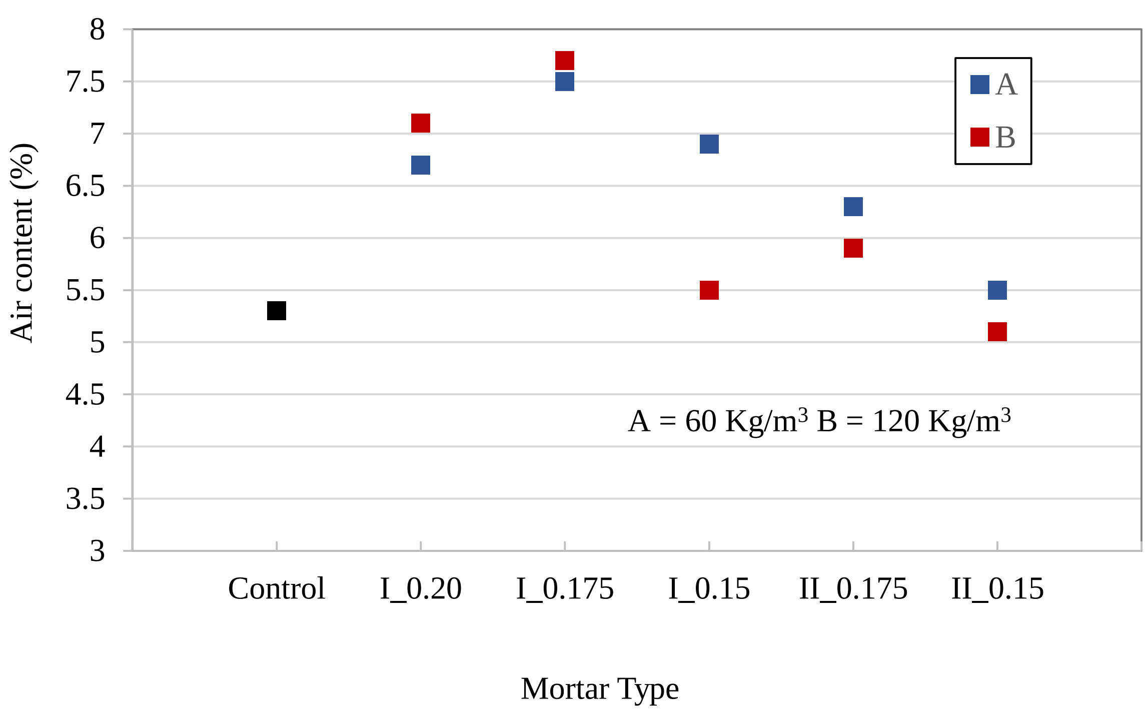


Figure 5.10 Air content measurement results for control and self-healing mortar

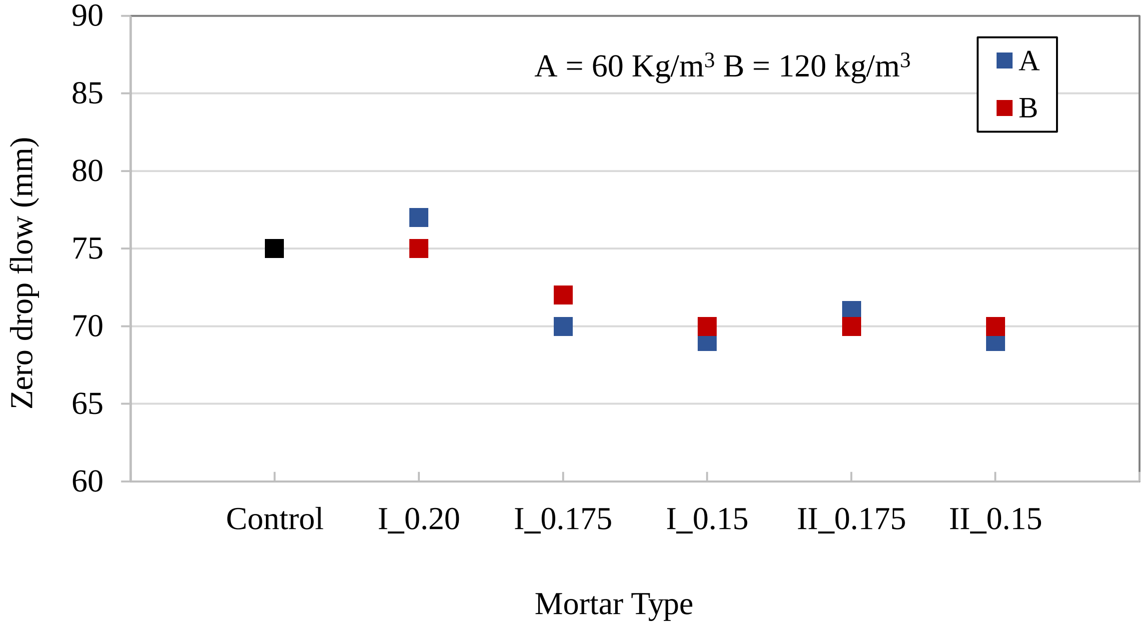


Figure 5.11 Flow measurement values for control and self-healing mortar

The zero drop flow values for the mortar are measured immediately after casting following the JIS R 5201 guidelines and the results are shown in Fig. 5.11. The experimental results show that the mortar flow values for I_0.20 granule case were approximately having same values with the control sample. The rest of the self-healing mortar samples exhibited a drop of about 5 mm flow value when compared with the control. This loss in flow values is natural and expected since the granules are finer in size than sand and they contain very little moisture inside them. However, this level of loss in flow values is assumed not so severe and could be taken care of by using superplasticizers in sensitive mixes where achieving the flow target is a priority

5.4 Effect of the granules on compressive strength of mortar samples

Fig. 5.12 presents the compressive strength developments of the control mortar and the self-healing mortar prepared by substituting sand by granules with reserved hydration potential inside them. The compressive strength measurements were conducted at the age of 7, 28 and 91 days after casting. It can be clearly seen that at the considered three measurement periods, the control specimen exhibited relatively higher strength than the self-healing samples. This is probably due to the presence of weak and only partially hydrated granules with in the mortar matrix.

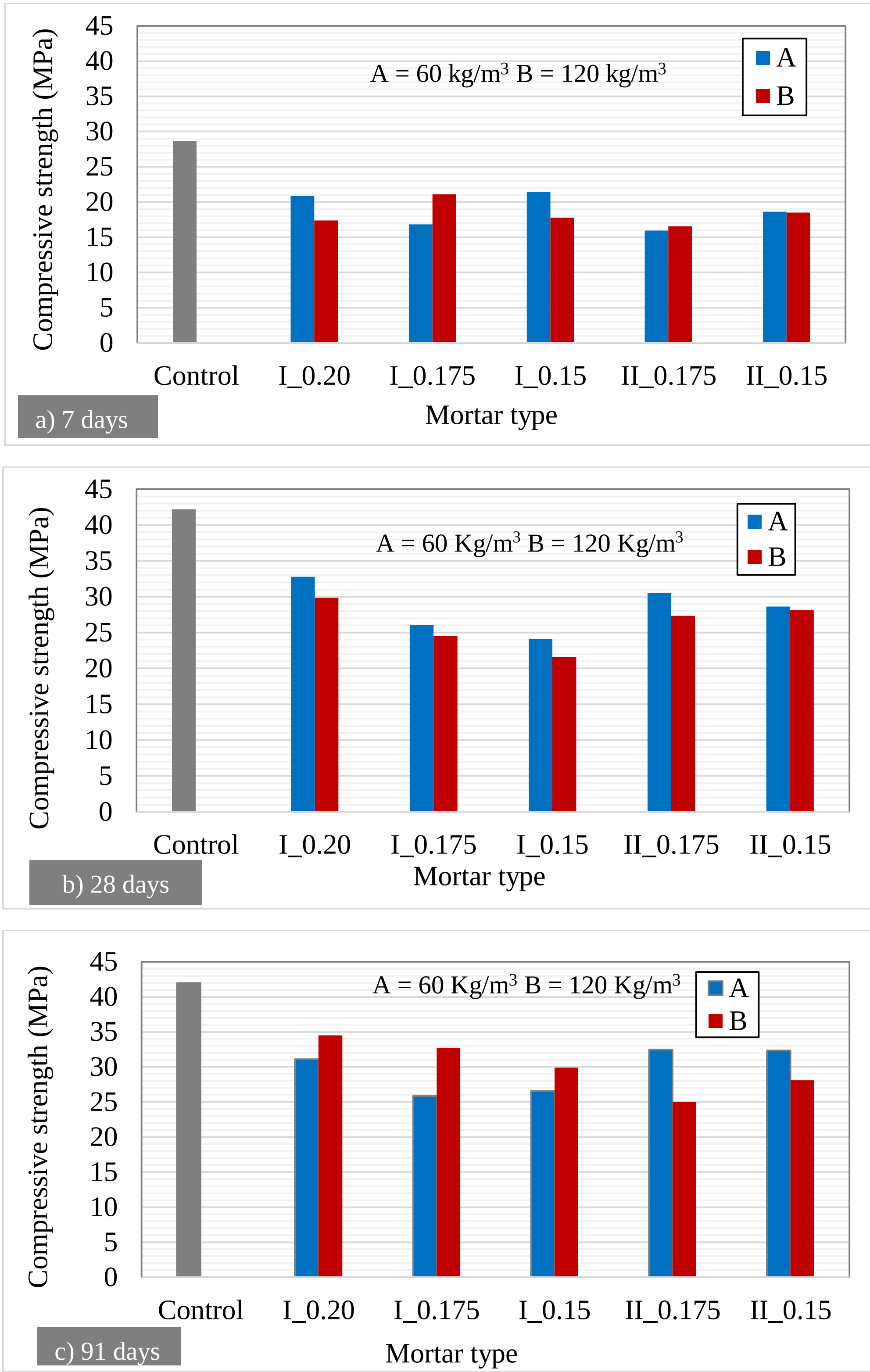


Figure 5.12 Compressive strength of control and self-heling mortar samples with granules with reserved hydration potential (a) at 7 days (b) at 28 days (c) at 91 days after casting

Considering the compressive strength development trend, the values for the control group increased from an average value of 28 MPa at 7 days to 42 MPa at 28 days and stabilized at the same value until 91 days age. The self-healing cases, on the other hand, could show strength development of an average of 5 MPa when the age varied from 28 to 91 days. This is probably due to the gradual hydration process and the related consumption of the water used to manufacture the granules even after 28 days.

However, the full potential hydration of the granules is not expected to happen since the cement particles inside them will be partially covered and protected by the coating liquid until crack happens and they become in contact with water. It is expected that even beyond the age of 91 days the compressive strength of the self-healing samples will be lower than that of the control sample with no granules. This concept will be described detail in separate section (section 5.8) in the following pages. For future applications, the compressive strength measurement beyond 3 months is highly recommended to be checked to confirm the potential reservation of the hydration capacity for the designed granules. Long-term tests up to 1 year could give better understanding of the strength development and the reservation of hydration potential for the granules indirectly.

5.5 TG-DTA test measurement results and the degree of hydration for mortar specimen

Thermogravimetric analysis was conducted to determine the extent of hydration of the cement paste with in the mortar matrix at the age of 110 days after casting. The mortar specimen were kept in sealed curing condition at a temperature of 20^0C until the test date. The chemically combined water content represented by the non-evaporable water is used as a measure of degree of hydration.

Initially, the cement paste powder was carefully extracted by crushing mortar specimen using hammer and grinding the crushed parts using mortar and pestle to pass 45 mm sieve and dried at 105^0C for 1 hour to remove the evaporable water. Up to 20 mg of the dried sample is weighed in a platinum crucible and then ignited from 30 to 1000^0C for 1 hour. The weight loss was continuously monitored through TG balance which was linked to a computer which recorded the data.

a = (Wi-Wn)/ Wn

where a is the ratio of combined water (mg/mg)

Wi is the weight of sample before ignition (mg)

Wn is the ignited weight of sample at 900^{0}C (mg)

Wi-Wn is the non-evaporable water,

The degree of hydration is determined by measuring the ratio of combined water at any stage divided by the total combined water for full hydration of cement which is considered as 0.23 for ordinary Portland cement [19, 23]. Accordingly, Fig 5.13 shows the estimations for the degree of hydration for control and self-healing granules prepared with granule dosage of 120 Kg/m^3 using this procedure . The individual thermogravimetric test results for each sample are presented in Fig. 5.14. The results show a significant rapid drop within temperature ranges of 420 - 500 ^{0}C which is due to decomposition of Calcium Hydroxide to calcium oxide and water (see Fig 5.14).

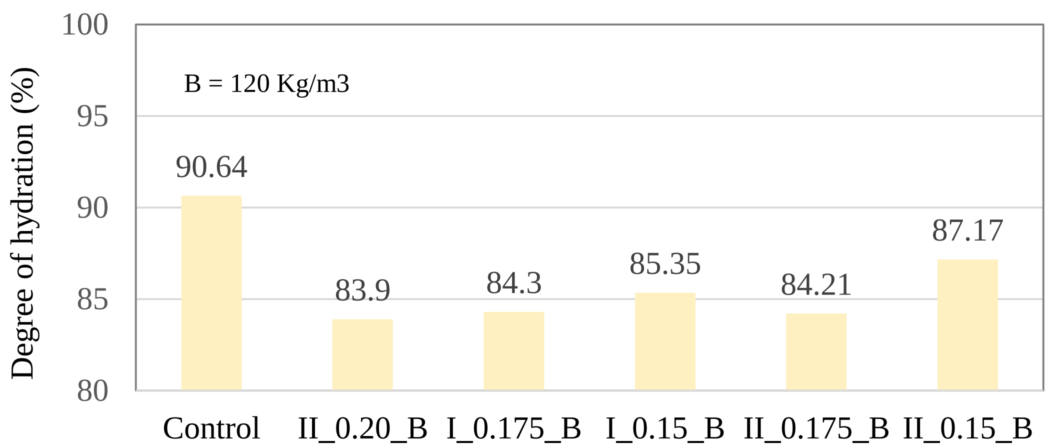


Figure 5.13 The degree of hydration for control and self-healing mortar at 110 days after casting

According to the results, the TG-DTA tests confirmed the control sample to show relatively higher degree of hydration than the self-healing mortar. A difference of approximately 7% is calculated for mortar containing II_0.20 granules while the minimum difference in hydration degree, approximately 2%, was observed for mortars made with II_0.20 (See Fig. 5.13). Over all hydration degree at this stage is very high (greater than 80%) for all samples since the water to cement ratio adopted for the mixes is 0.5. In reality, nevertheless, better reservation of hydration degree could be achieved with designing mixes with low water to cement ratios. In low water to cement ratio concrete mixes the cement matrix will contain large amount of unhydratred cement which contribute to the natural self-healing process when crack occurs. Yet, in this study it was necessary to minimize the natural self-healing process by adopting higher water to cement ratio and to examine the contribution of granules for crack self-healing process.

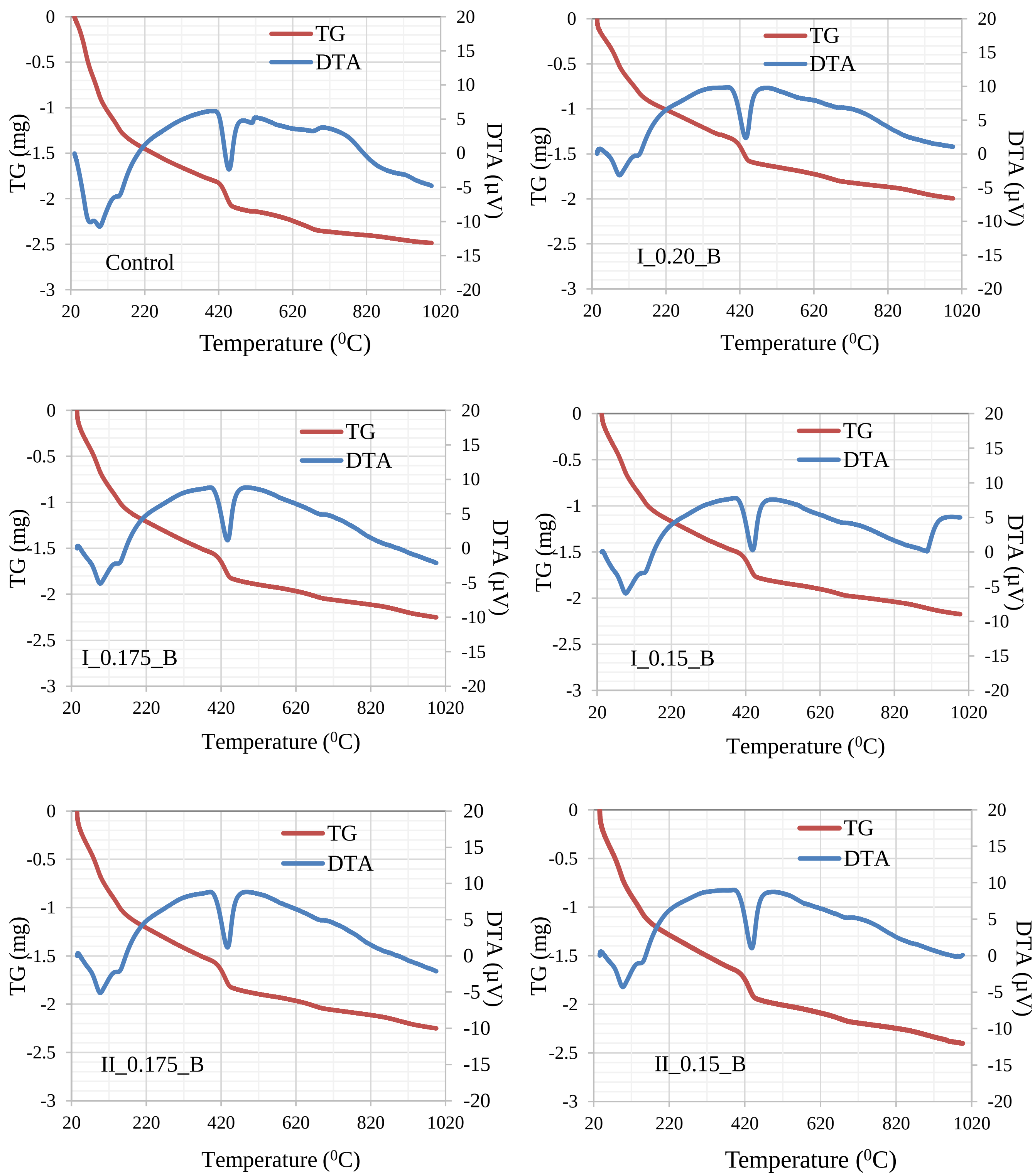


Figure 5. 14 TG-DTA test results for control and self-healing mortar at 110 days after casting

5.6 Water pass test results

5.6.1 28 days old mortar samples

Fig. 5.15 presents the average flow measurements in gm/s for 28 days old specimen at average crack width provision of 0.2 mm for mortar made with Type I granules and Type II granules. The results show that initial flow values for all samples exhibited rapid drop for up to 5 to 7 days after the start of water pass test. After the 7th day this flow rate is observed to have gradual reduction up until the 14th day water flow measurements (see Fig 5.15 (a) and (b)).

At the end of the 14th day, 28th day and 56th days secondary stage vacuuming was conducted according to the procedures described in section 3.2.1. This step resulted in revival of the water flow values. The observed increase in water flow measurement is likely due to the removal of the entrapped air bubbles inside the crack gap during water flow measurements. After the vacuuming at each stage the flow values for self-healing mortar samples showed lower water flow rate than the control sample at each stage (see Fig 5.15 (a) and (b)). This is as considered as a positive outcome indicating the crack closing, thereby the flow reduction, due hydration product formation from the granules is effectively advantageous over the control samples.

Considering the time duration of the water pass test the self-healing samples with type two (OPC + SF) type granules could reach to a value of approximately zero. The mortar samples II_0.175 A and II_0.15 B exhibited the lowest water flow values even after vacuuming at the end of the 56th day. As a general trend it was observed that the amount of rise in flow due to vacuuming to gradually decrease when the test dates changed from 14 to 28 to 56th day. This fact is related to gradual closing of crack gaps by the formation of products sealing the crack with elapse of time.

In order to better compare the self-healing ability of each sample, the 0th day initial water flow values are compared with the respective values at the end of the 14th and 28th day of the water flow measurements. This comparison is done both before vacuuming and after conducting vacuuming the considered stages. Fig. 5.16 summarizes the water flow reduction in % for 28 days old mortar specimen at average crack width provision of 0.2 mm (a) at the 14th day of water pass test (b) at the 28th day of water pass test. The presented values in percentage are the results of averaged flow reduction for three specimen for each sample. Figure 5.16 (a) shows that at the values of the average water flow re reduction at the end of 14 days of water pass test before vacuuming was

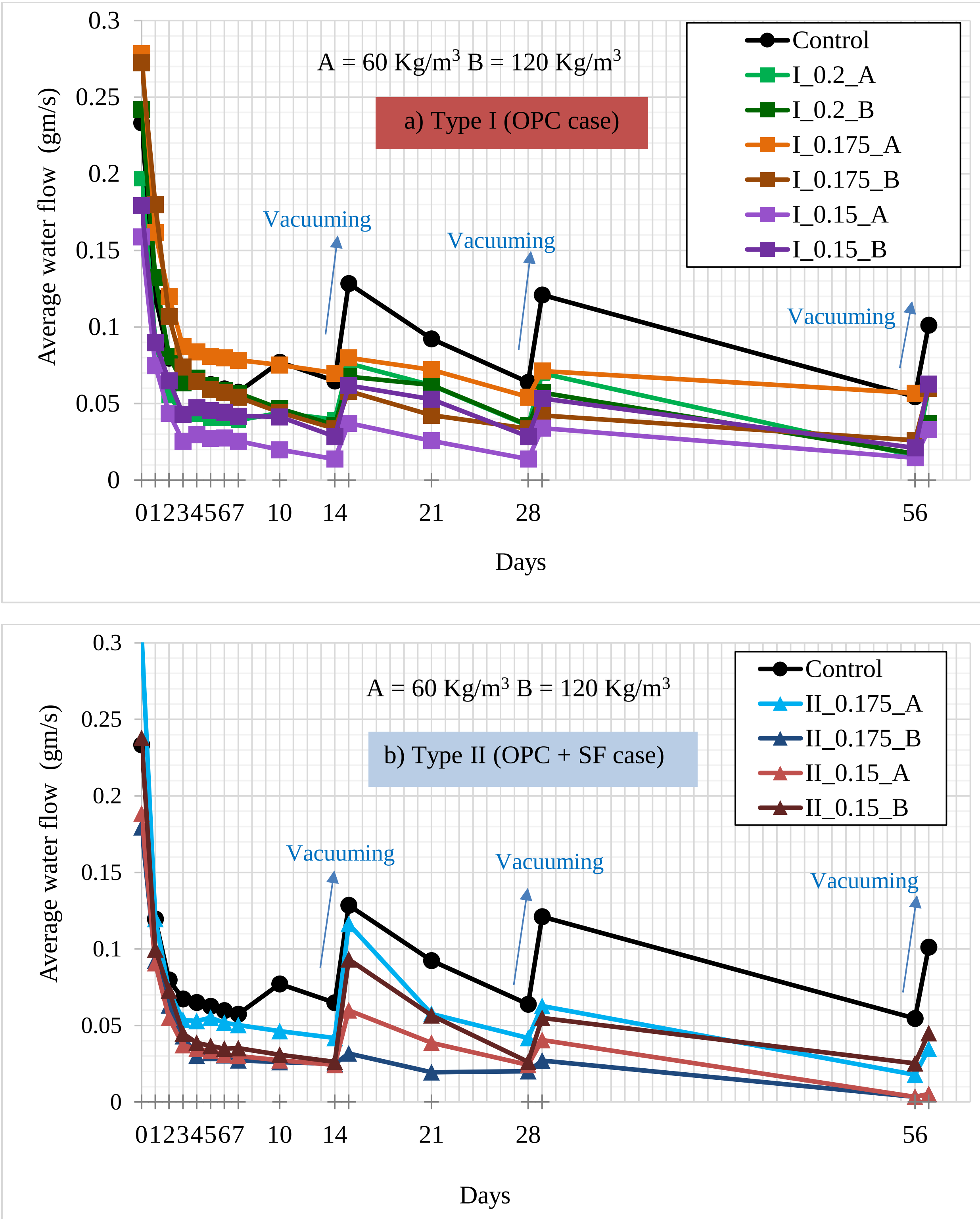


Figure 5.15 Water flow measurements for 28 days old specimen, crack width = 0.2 mm (a) Type I granules, (b) Type II granules

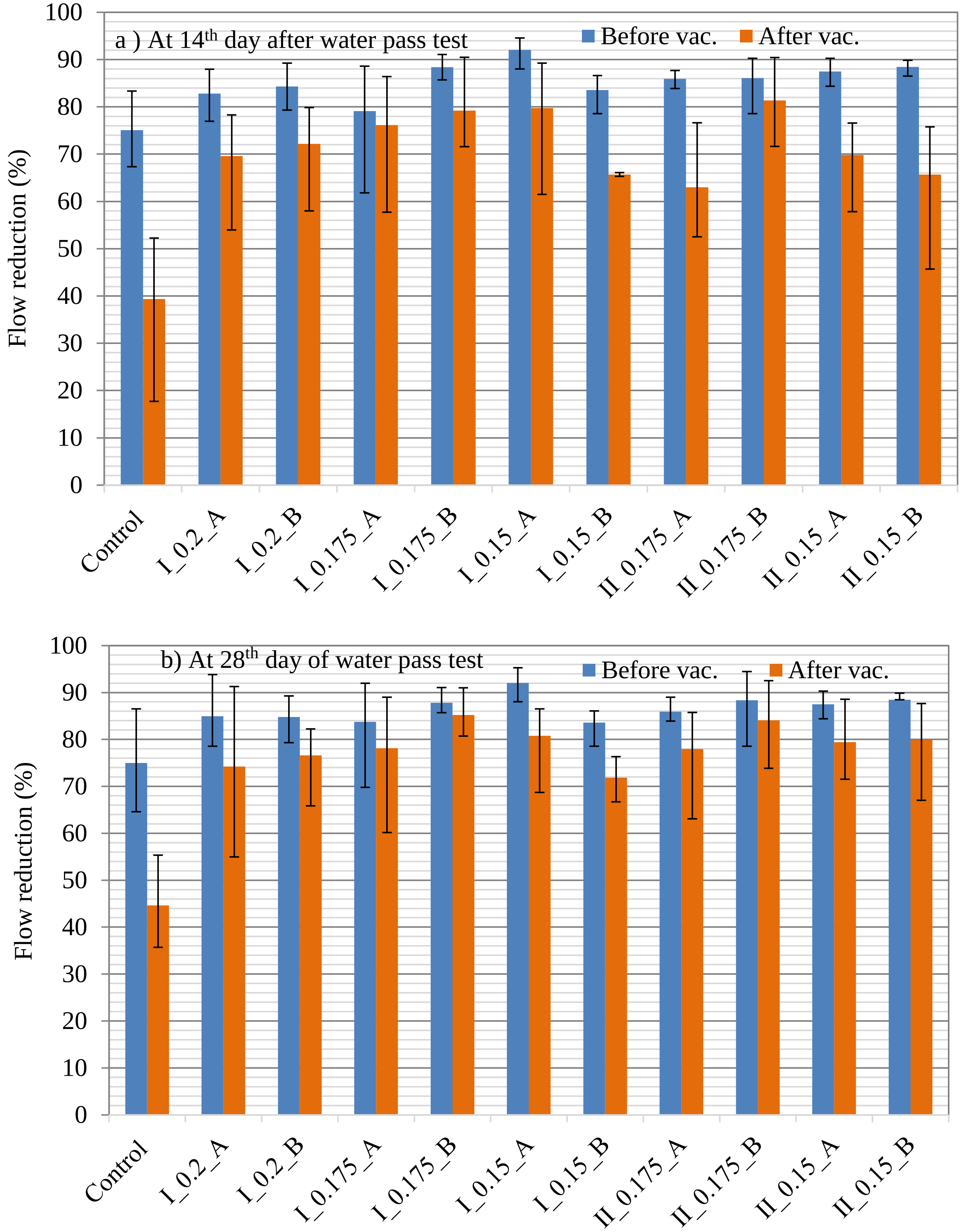


Figure 5.16 Water flow reduction for 28 days old mortar specimen , crack width = 0.2mm (a) at the 14th day of water pass test (b) at the 28th day of water pass test

approximately 75 % for control cases while the self-healing mortar could achieve values ranging from minimum of 80% for I_0.175_A to maximum of 92 % for I_0.15_A. Upon vacuuming the flow reduction value reached about 40 % for the control case where as the self-healing mortar group could exhibit a minimum of 62% for II_0.175_A to a maximum of 80% for I_0.15_A respectively at the end of the 14^{th} day (see Fig. 5.16 (a)).

Considering the results of flow reduction at the end of 28^{th} day, the flow reduction value before vacuuming was approximately 75 % for control cases while the self-healing mortar could achieve values ranging from minimum of 80% by I_0.175_A to maximum of 92 % by I_0.15_A. Upon vacuuming the flow reduction value reached about 44 % for the control case where as the self-healing mortar group could show a minimum of 72% for I_0.175_A to a maximum of 85 % for I_0.175_B respectively at the end of the 14^{th} day (see Fig. 5.16 (b)).

In general, the self-healing mortar samples showed higher flow reduction at the age of 14^{th}, 28^{th} and 56^{th} day of the water pass test compared to the control sample for crack width of 0.2 mm. Comparing the effect of granule type the effect of the difference in material composition between Type I and Type II was not clearly visible until the 28^{th} day of water pass test. At long term tests of 56^{th} day, however, inclusion of the Type II granules brought about nearly zero water flow reduction (see Fig. 5.15b) likely due to the continuation of pozzolanic reaction of the Silica fume. Comparing the dosage rates of granules, marked differences in flow reduction are not exhibited when the dosage increased to from 60 kg/m^3 to 120 Kg/m^3 for the same granule type (see Fig 5.16 (a) and (b)). At this stage the up to a maximum of 85 % water flow reduction was achieved at the end of the 28^{th} day of the water pass test for 28 days old samples with crack width of 0.2 mm (see Fig 5.16 (b)).

Fig. 5.17 shows the average flow measurements in gm/s for 28 days old specimen at average crack width provision of 0.3 mm for mortar made with Type I granules and Type II granules. The results revealed that initial flow values for all samples exhibited rapid drop the first 7 days after the start of water pass test. After the 7^{th} day this flow rate is observed to have gradual reduction up until the 14^{th} day water flow measurements (see Fig 5.17 (a) and (b)).

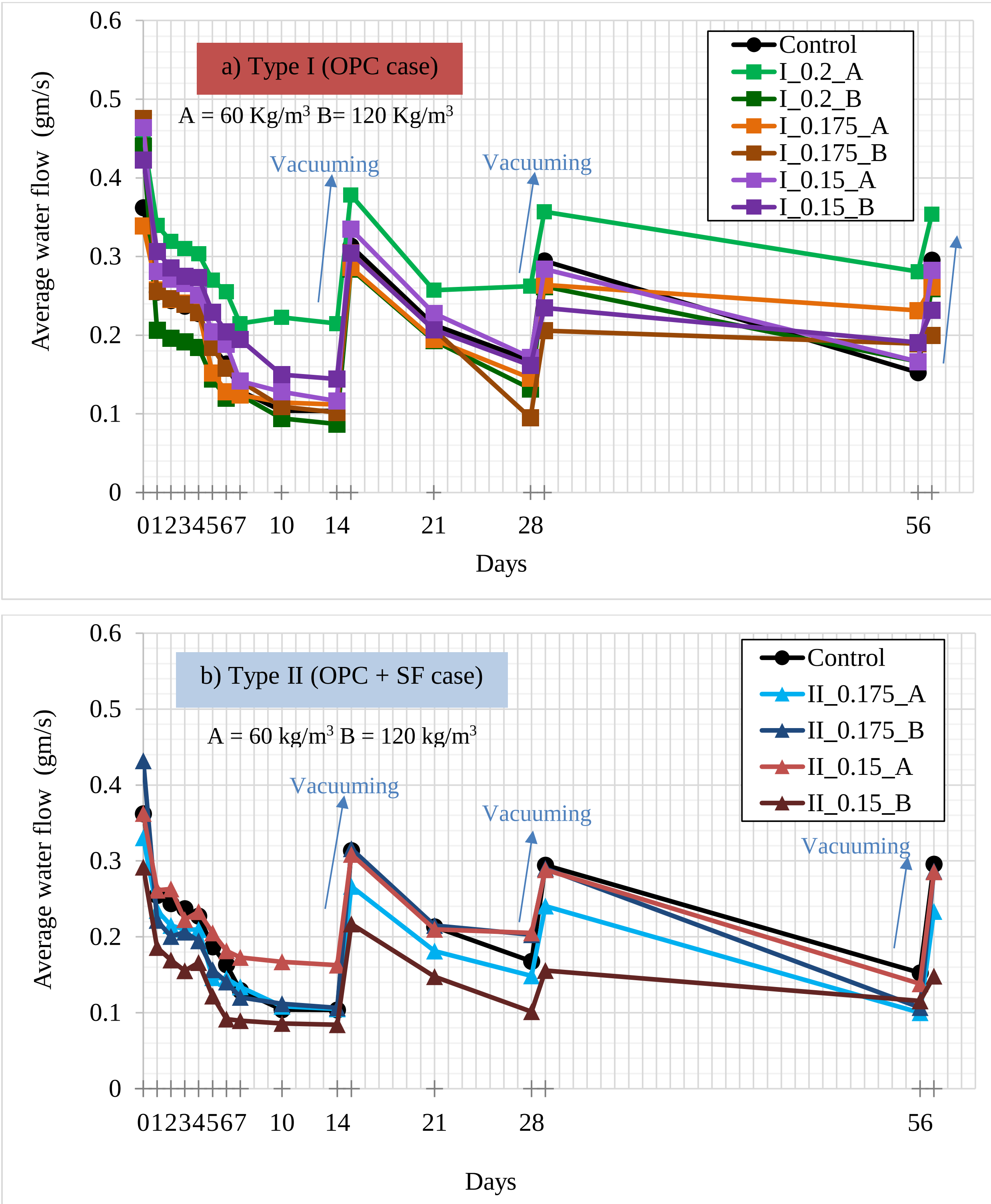


Figure 5. 17 Water flow measurements for 28 days old specimen, crack width = 0.3 mm (a) Type I granules, (b) Type II granules

At the end of the 14^{th} day, 28^{th} day and 56^{th} days secondary stage vacuuming was conducted according to the procedures described in section 3.2.1. This step resulted in marked revival of the water flow values for most samples. The observed increase in water flow measurement is likely due to the removal of the entrapped air bubbles inside the crack gap during water flow measurements. After the vacuuming at each stage the flow values for self-healing mortar samples some of the samples showed similar flow value as the control sample. (see Fig 5.17 (a) and (b)). This result indicates that crack width of 0.3 mm is relatively wide and ambitious target to fully close by mere action of the added granules at the applied dosage rates of 60 and 120 Kg/m^3 of mortar.

So as to compare the self-healing ability of each sample, the 0^{th} day initial water flow values are compared with their respective values at the end of the 14^{th} and 28^{th} day of the water flow measurements. This comparison is done both for before after conducting vacuuming for each of the samples. Fig. 5.18 summarizes the water flow reduction in % for 28 days old mortar specimen at average crack width provision of 0.3 mm (a) at the 14^{th} day of water pass test (b) at the 28^{th} day of water pass test. The presented values in percentage are the results of averaged flow reduction values for three specimen for each sample.

Figure 5.18 (a) reveals that at the values of the average water flow reduction at the end of 14 days of water pass test before vacuuming was 70 % for the control sample while the self-healing mortar exhibited flow reduction rate ranging approximately from 54% to 78%. These values were significantly reduced after vacuuming. The control sample had only 13% water flow reduction and the self-healing samples had a minimum value of 14% and a maximum flow reduction of 36% at the 14^{th} day.

At the end of the 28^{th} day water pass test the control specimen exhibited flow reduction of 50% before vacuuming while the self-healing samples showed values ranging from 42% to 80% before vacuuming (see Fig 5.18 (b)). Here, comparing the 28^{th} day values to the 14^{th} day flow reduction before vacuuming, it is observed they are lower than their respective values at the test stage of 14^{th} days. Air bubble generation/entrapment/ and related flow reduction till the 28^{th} day is expected to be low at crack width of 0.3 mm once the vacuuming is conducted at the 14^{th} day. After vacuuming is conducted at the 28^{th} day, the control samples had a flow reduction of 20% and the self-healing samples exhibited a minimum flow reduction value of 20 to a maximum of 56% at the 28^{th} day.

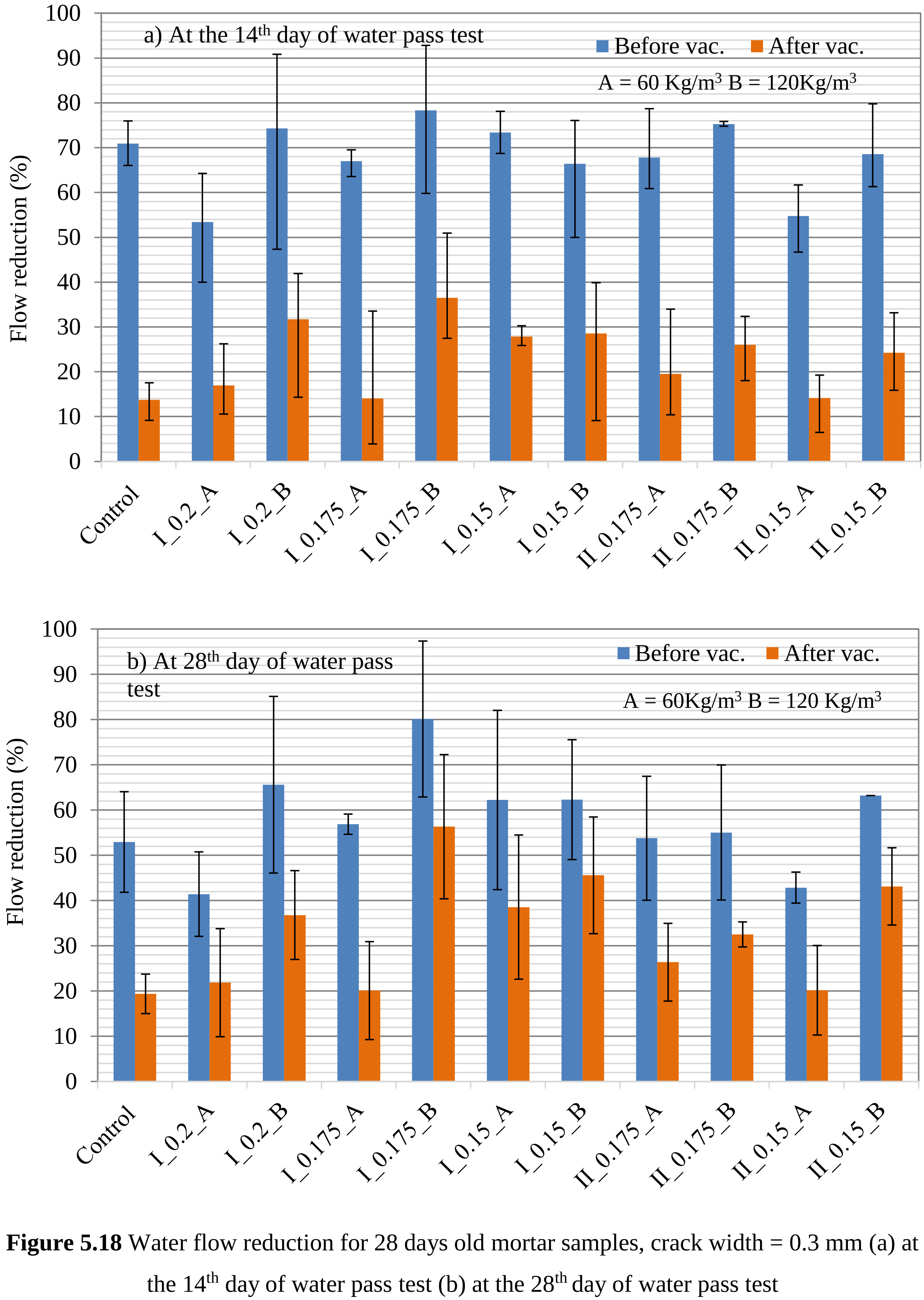


Figure 5.18 Water flow reduction for 28 days old mortar samples, crack width = 0.3 mm (a) at the 14th day of water pass test (b) at the 28th day of water pass test

Here it is interesting to note the trend of water flow reduction for self-healing samples and their respective granule dosage rates. According to the results, almost all self-healing specimen with the higher granule dosage performed better in reducing the water flow compared to their respective samples with lower granule dosage. It is inferred that the granule dosage rate becomes important influencing factor for crack closure at such large crack widths of 0.3 mm or higher. At the applied dosage rates of 60 and 120 Kg/m^3, however, crack width of 0.3 mm was a severe case to reach full crack closure (see Fig 5.18).

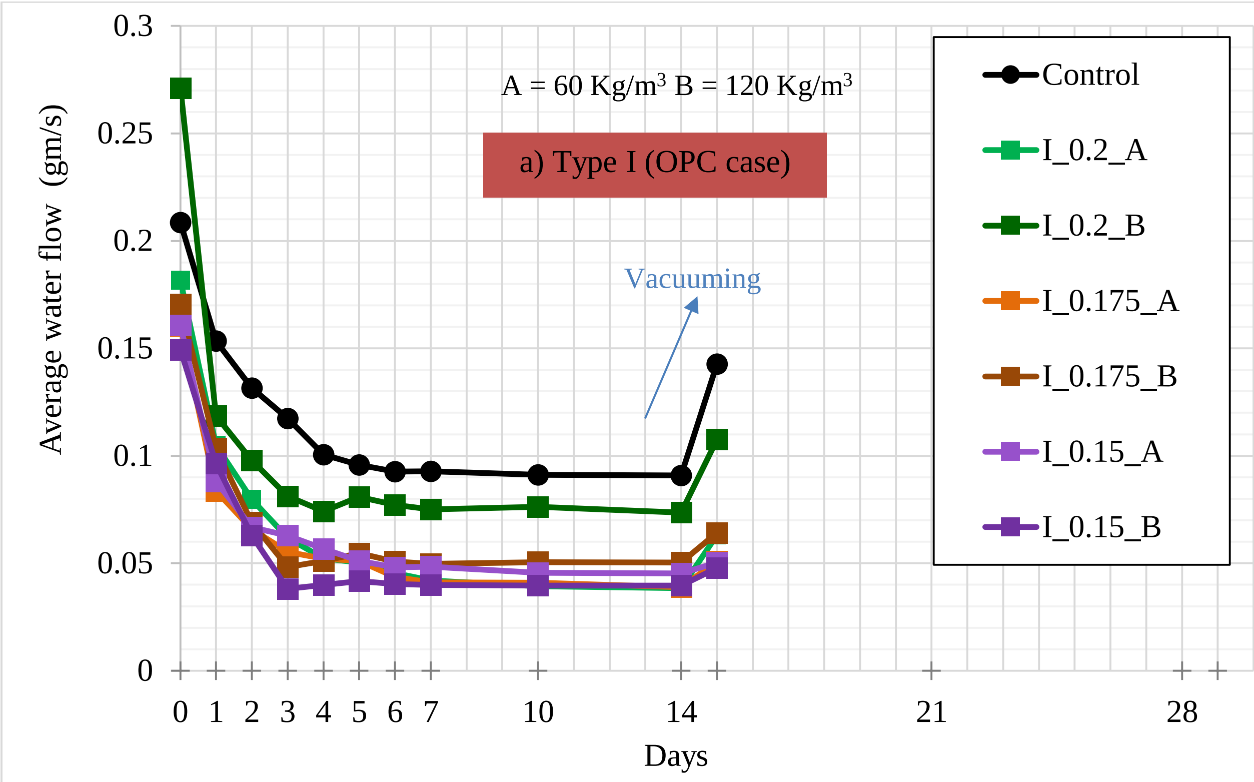
Accordingly, it is highly recommended that the use of granules should be combined with crack width limiting techniques such as inclusion of fibers to bring about better self-healing performance in concrete. In addition, to achieve full crack closure not only OPC and SF but also other material combinations such as expansive and swelling agents as recommended by Ahn (2007) might help reach the target.

5.6.2 91 days old mortar samples

Water flow measurements for 91 days old specimen of average crack width 0.2 mm for control samples as well as for self-healing mortar with Type I and Type II granules are presented in Fig. 5.19. Similar to the cases of 28 days old samples, the results show that initial flow values for all samples exhibited rapid drop for the first 7 days after the start of water pass test. After the 7^{th} day this flow rate is observed to have gradual reduction up until the 14^{th} day water flow measurements (see Fig 5.15 and Fig 5.19).

Additionally, Fig 5.20 reveals the water flow measurements for 91 days old samples of average crack width of 0.3 for control and self-healing mortar samples with Type I and Type II granules. According to the results, it is observed that the water flow value decrease with a rapid drop for the first 7 days of the water pass test and exhibit gradual decrement afterwards until the 14^{th} day.

Considering the age of specimen and its effect on the flow reduction, it was observed that the minimum flow values exhibited by both samples with crack width of 0.2 mm and 0.3 mm were lower for the 28 days old samples than for the 91 days old samples. For 28 days old samples the minimum water flow rate achieved by the samples with average crack width of 0.2 mm is less than 0.05 gm/s before14^{th} day vacuuming was conducted (see Fig 5.15 (a) & (b)). It can be seen that the minimum water flow rate for those samples was achieved by I_0.15_A having water flow value of 0.1gm/s just at the 14^{th} day (Fig 5.15 (a)).



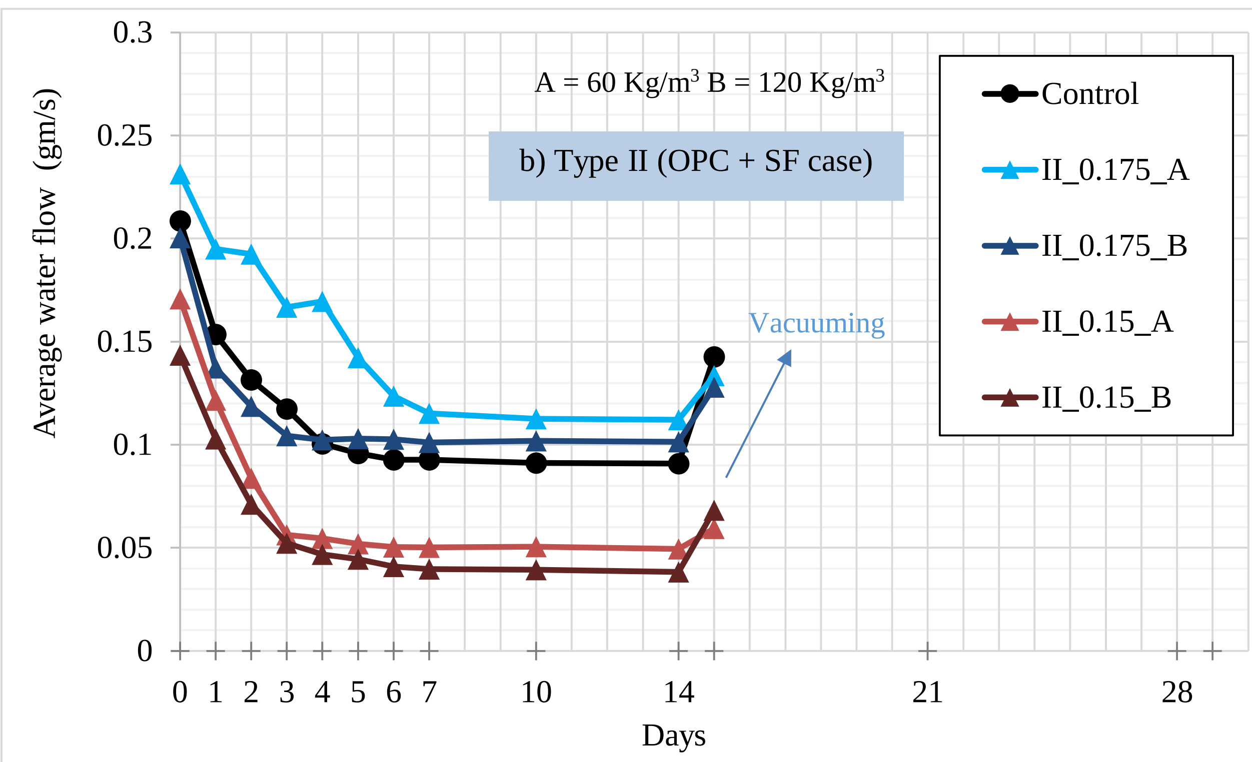
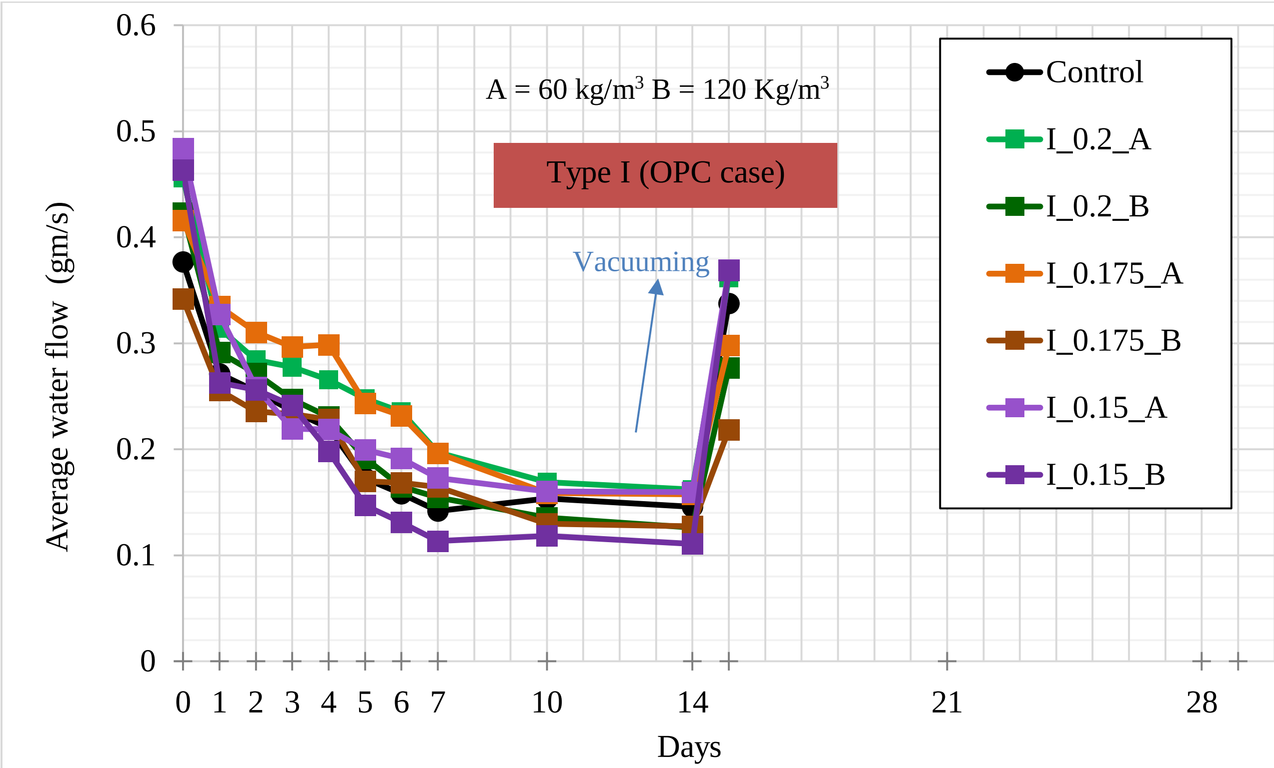


Figure 5.19 Water flow measurements for 91 days old specimen, crack width = 0.2 mm (a) Type I granules, (b) Type II granules



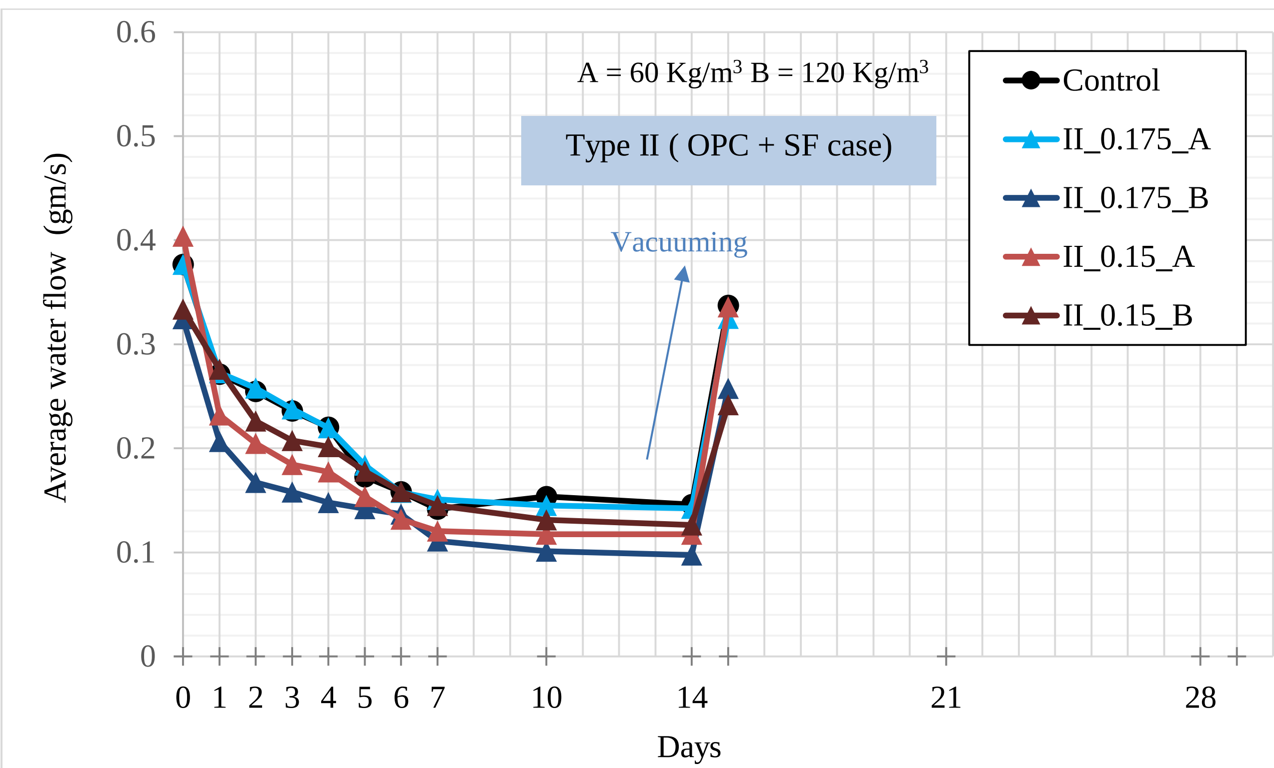


Figure 5.20 Water flow measurements for 91 days old specimen, crack width = 0.3 mm (a) Type I granules, (b) Type II granules

On the other hand, the for the 91 days old samples this water minimum flow value achieved by the self-healing mortar is relatively higher. For average crack width of 0.2mm, Fig 5.19 (a) and (b) show that the minimum flow value just before conducting vacuuming at the 14th day was 0.4 gm/s equally achieved by I_0.15_B, I_0.175B and II_0.15B.

In summary the younger the younger specimen performed better for crack closing process within the considered time duration of 14 days. The compressive strength values for the control group increased from an average value of 28 MPa at 7 days to 42 MPa at 28 days and stabilized at the same value until 91 days age. The self-healing cases, on the other hand, could show strength development of an average of 5 MPa when the age varied from 28 to 91 days (see Fig. 5.12). It is expected that this gain in strength by the self-healing samples is related to the self-heling ability reduction with age. This loss in self-healing ability with age is probably due to the gradual hydration process and the related consumption of the water used to manufacture the granules even after 28 days.

However, the full potential hydration of the granules is not expected to take place since the cement particles inside them will be partially covered and protected by the coating liquid until crack happens and they become in contact with water. It is expected that even beyond the age of 91 days the reserved hydration potential of the self-healing samples will be higher than that of control sample with no granules. At this study TG-DTA test at the 110th day after casting have revealed that there still remains higher amount of unhydratred cement in the self-healing samples compared to the control sample with no granules (see Fig 5.13). For future applications, the water flow reduction measurement beyond 3 months is highly recommended to be checked to confirm the potential reservation of the hydration capacity and there by the self-healing performance for the designed granules. Long-term tests up to 1 year could give better understanding of the strength development and the reservation of hydration potential and self-healing ability for the granules made with the coating liquid.

Fig 5.21 presents the water flow reduction summary for 91 days old mortar samples at the 14th day of water pass test for mortar samples with average crack width of 0.2 mm and 0.3 mm. Considering the results of flow reduction for crack width of 0.2 mm at the end of the 14th day, the flow reduction value before vacuuming was approximately 58 % for control cases while the self-

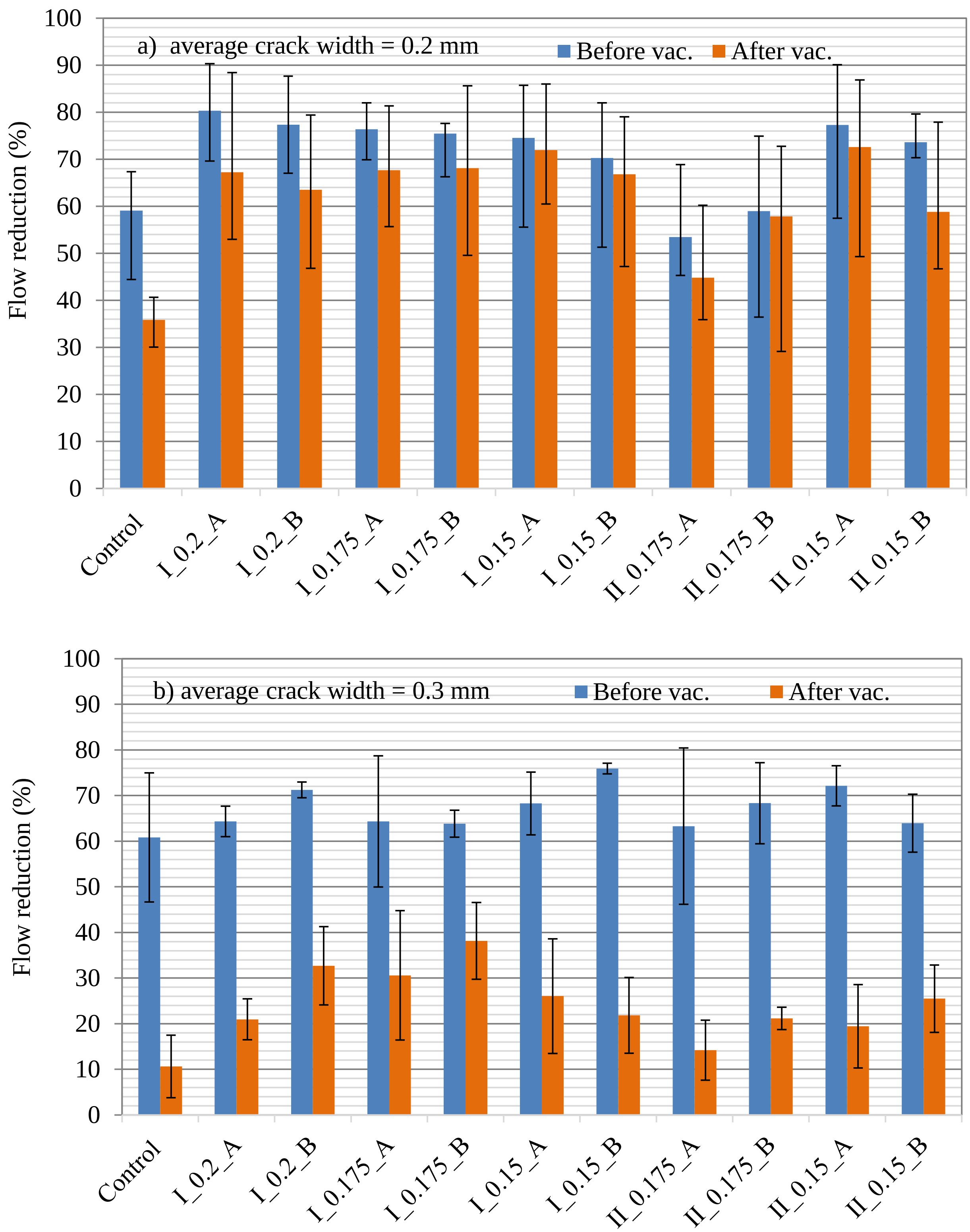


Figure 5.21 Water flow reduction for 91 days old mortar samples at the 14th day of water pass test (a) mortar samples with average crack width of 0.2 mm (b) average crack width of 0.3 mm

healing mortar could achieve values ranging from minimum of 54 % by II_0.175_A to maximum of 80 % by I_0.2_A. Upon vacuuming the flow reduction value reached about 36% for the control case where as the self-healing mortar group could show a minimum value of 45% for I_0.175_A to a maximum of 72 % for I_0.15_A and II_0.15_B at end of the 14^{th} day (see Fig. 5.21 (a)).

At crack width of 0.3 mm, the 91 days old control specimen exhibited flow reduction of 60% before vacuuming. The self-healing mortar samples had a minimum flow reduction of 64 % equally achieved by I_0.2_A, I_0.175_A, I_0.15_B, I_0.175A and I_0.15_B. The maximum flow reduction before vacuuming at the 14^{th} day was I_0.15_B 76%. After vacuuming, the flow values dropped significantly to a minimum of 14% by II_0.175_A to maximum 38% by I_0.175_B. Comparing to the control specimen which had flow reduction of 10% after vacuuming all the self-healing samples still had relatively better self-healing performance (see Fig. 5.21(b)).

Here it is interesting to note the trend of water flow reduction for self-healing samples and their respective granule dosage rates. According to the results, almost all self-healing specimen with the higher granule dosage performed better in reducing the water flow compared to their respective samples with lower granule dosage for crack width of 0.3 mm. It is inferred that the granule dosage rate continues to be important influencing factor for crack closure even at later ages for large crack widths of 0.3 mm or higher. At the applied dosage rates of 60 and 120 Kg/m^3, however, crack width of 0.3 mm was a severe case to reach full crack closure (see Fig 5.21 (b)). Hence, it is highly recommended that crack width limitation and use of other materials be considered for future studies.

5.7 Crack closing process

Figures 5.22 and 5.23 compare the bottom surface cracks at marked locations for the control and self-healing samples at the start and end of the water pass test. The samples in the left side show the control samples at 0^{th} day and 56^{th} day while at the right side the self-healing samples with Type I and Type II granules are presented. At the last bottom section the observation with the higher magnification for the 56^{th} day results are presented. It can be clearly seen from the microscopic observations that all the specimens had white crystalline products at the crack gaps at the end of the test period. Comparing the self-healing mortar samples with the control more product

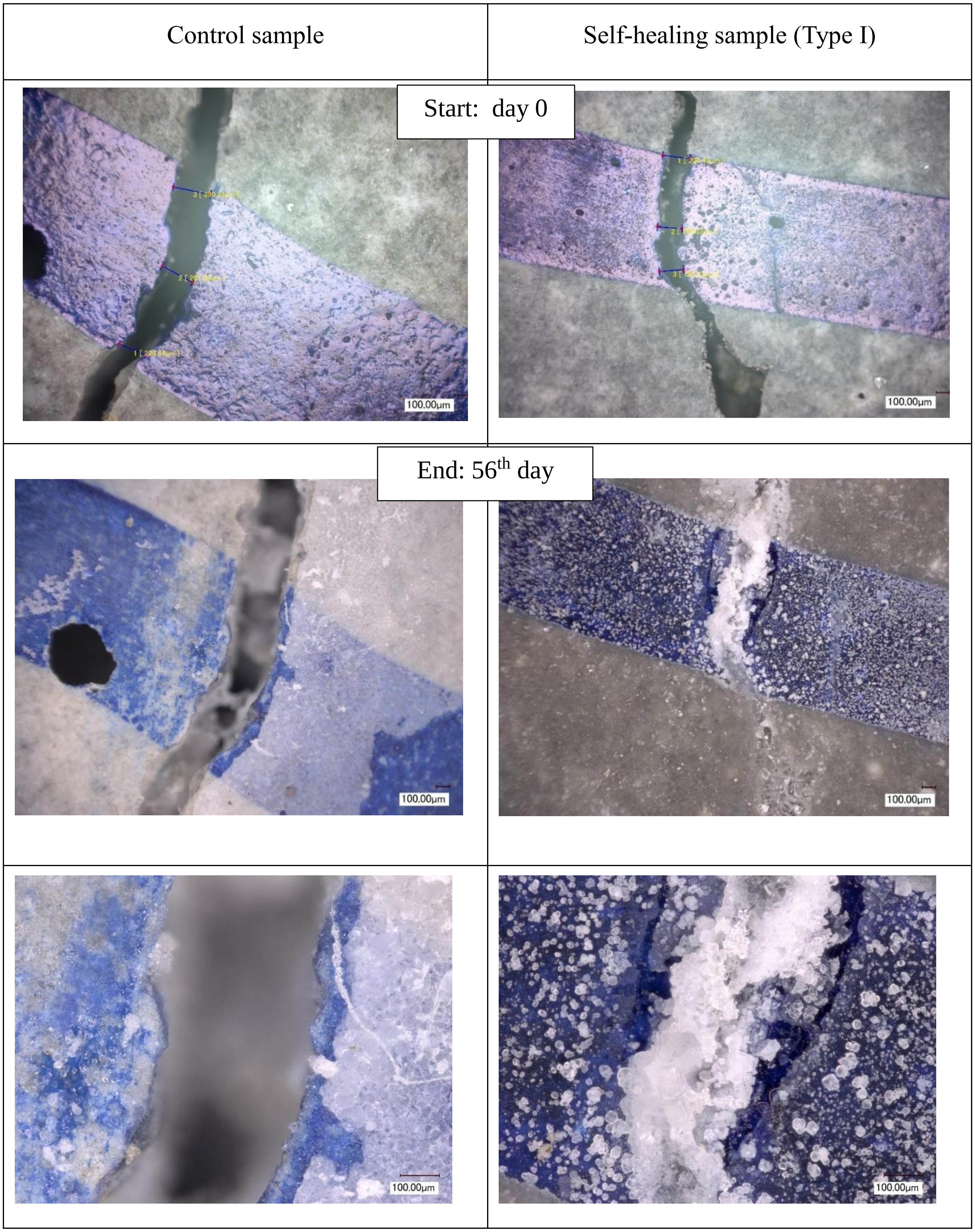


Figure 5.22 Bottom crack width observations for by microscope at the start (0th day) and at the end of water pass tests (56th day) for 28 days old specimen

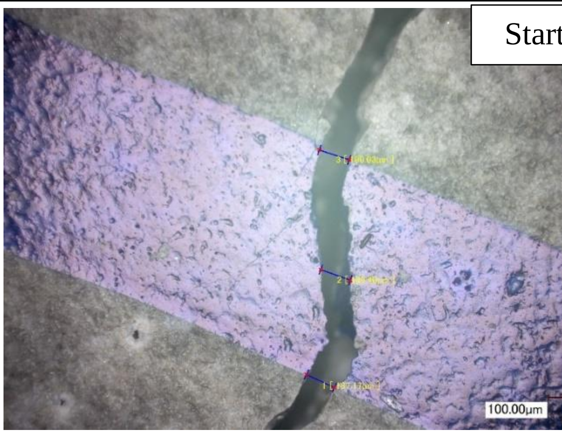
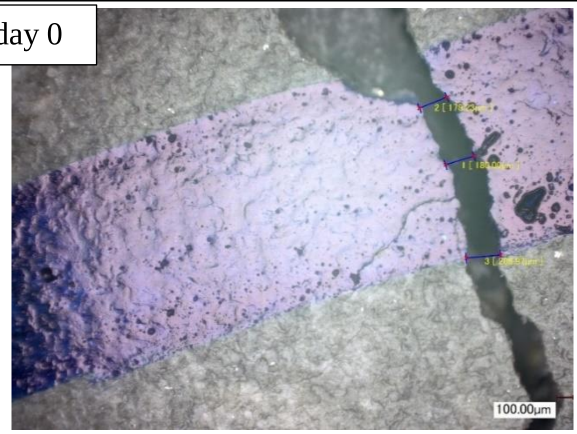
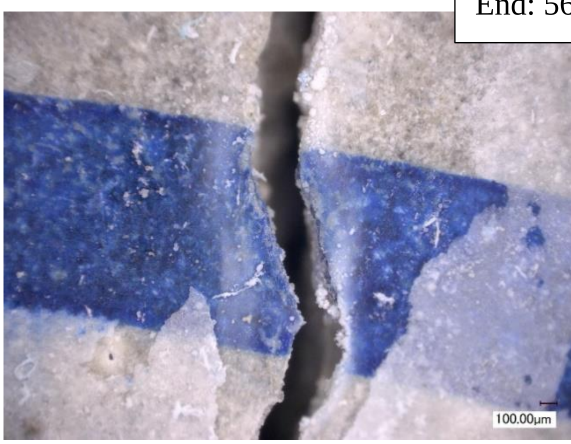
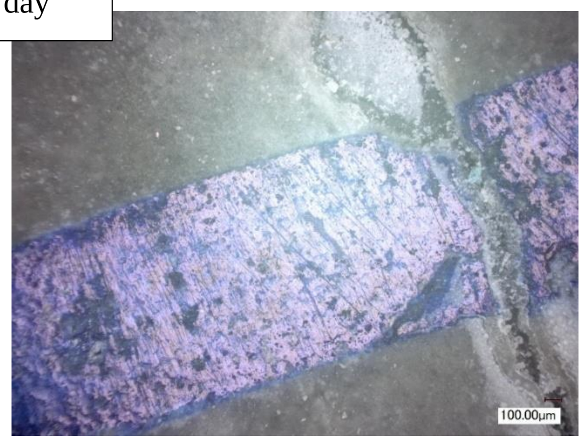
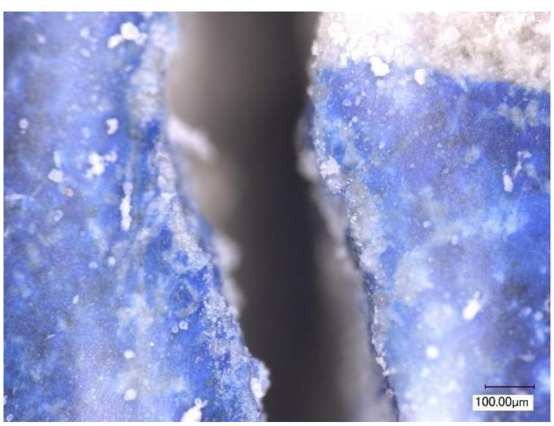
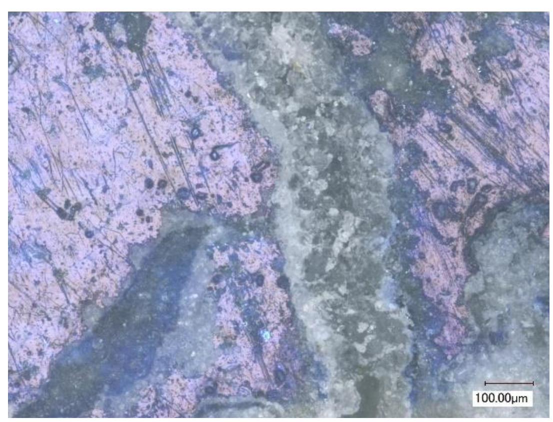
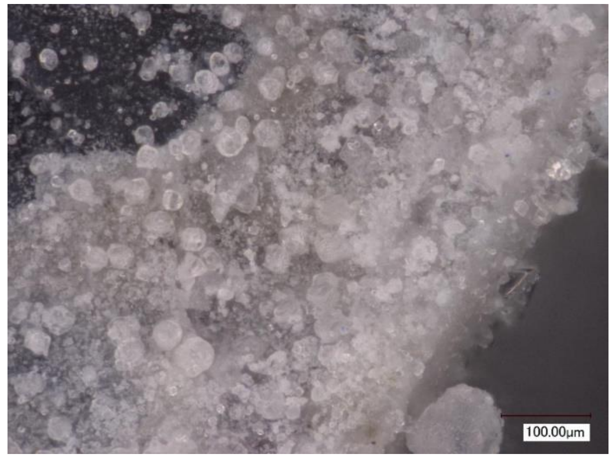
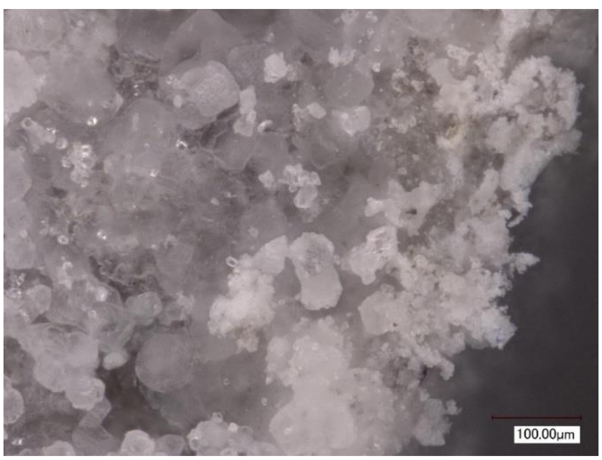
Control sample	Self-healing sample (Type II)
Start: day 0	
	
End: 56th day	
	
	

Figure 5.23 Bottom crack width observations for by microscope at the start (0^{th} day) and at the end of water pass tests (56^{th} day) for 28 days old specimen

a) Location of crack surface observation



b) Control sample



c)Self-healing sample (Type I)

d) Self-healing sample (Type II)

Figure 5.24 Crack surface observations for by microscope at the and at the end of water pass tests (56th day) for 28 days old specimen.

formation is observed for the self-healing samples than for the control samples. And this more product formation is associated with better flow reduction exhibited by the self-healing mortar.

Fig. 5.24 presents microscopic observations at the crack surface once the specimen are re-opened at the end of the water pass test (56th day) for 28 days old samples. Fig 5.24 (b) shows that the control sample had relatively smaller size and widely dispersed crystals on the surface. While as can be seen from Fig 5.24 (c) and (d) that the self-healing mortar made by granules with reserved hydration potential had denser and larger sized products. Larger crystal sizes for self-healing mortar made by using coating liquid have been similarly reported by Meta (2018).

5.8 Concept behind granules with reserved hydration potential

The compressive strength development trend has shown that the samples with the manufactured granules are lower in strength than those without the self-healing additives (see Fig 5.12). These granules are expected to be the weakest components there by causing the observed strength reductions in the matrix while being only partially hydrated and containing large amount of unhydratred cement particles in side them. TG-DTA tests have also confirmed the presence of more unhydratred particles for samples with granules since the at the 110th day after casting the hydration degree was revealed to be lower in the self-healing samples when compared to the control sample with no granules (see Fig 5.13).

Fig 5.25 (A) illustrates the conceptual understanding of the granules at early stages after casting (1 month and prior). At this initial manufacturing stage the cement particles are agglomerated by a mixture of water and coating liquid using mortar mixer. The cement particles are expected to be bonded by thin layer of hydration products and small amount of the liquid mixture will be surrounding the granules. And this state is expected to continue after mixing for the first few weeks.

As the time progresses the water contained in the granules will be gradually consumed for the hydration process of the cement particles while the non-reactive coating liquid remains surrounding the cement agglomerates (see Fig 5.25 (B)). This conceptual understanding of the gradual slow hydration could be related with the continued strength developments of mortar incorporating the granules even beyond 28 days. Fig 5.12 (b) and (c) show that the compressive strength of the control and self-healing samples in which strength increments up to 5 MPa were observed for the samples with granules. This strength development is expected to be due to the gradual the hydration of the granules.

However, the full potential hydration of the granules is not expected to take place since the cement particles inside them will be partially covered and protected by the coating liquid until crack happens and they come in contact with water. The coating liquid is expected to protect the granules from direct contact with the concrete mixing water. Thus, it is expected that even beyond the age of 91 days the reserved hydration potential of the self-healing samples will be stable once the water used to manufacturing them is consumed as shown in Fig 5.25 (B). Once crack occurs and water flow takes place, the coating liquid will get washed out by the action of running water and further rehydration of the granules will bring about crack closure.

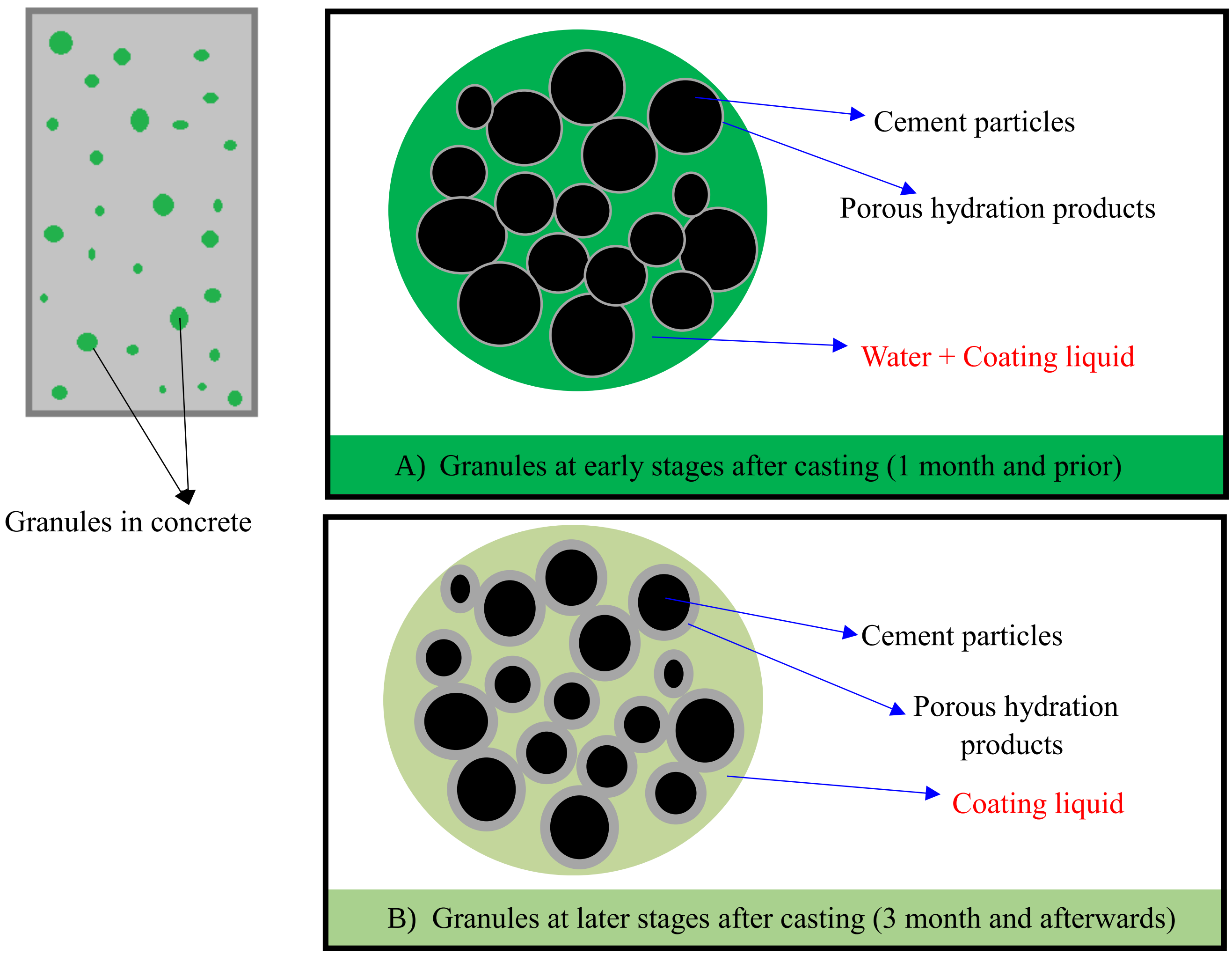


Figure 5.25 Conceptual understanding of the granules with reserved hydration potential at early and later stages

Based on this understanding, it is recommended that lower w/c should be adopted for making self-healing concrete to use the coating liquid to its potential ability and to avoid the hardening of the granules. In such ideally designed self-healing concrete mixture cement agglomerates shall remain protected from the mixing water by the coating liquid. And once crack occurs the porous hydration products that surround the particles can let ion and water exchange and further rehydration of the cement particles.

Over all hydration degree achieved by the samples in this study is considered very high (greater than 80%) for all samples since the water to cement ratio adopted for the mixes is 0.5 (see Fig 5.13). In reality, nevertheless, better reservation of hydration degree could be achieved with designing mixes with low water to cement ratios. In low water to cement ratio concrete mixes the cement matrix will contain large amount of unhydratred cement which contribute to the natural self-healing process when crack occurs. Yet, in this study it was necessary to minimize the natural self-healing process by adopting higher water to cement ratio and to examine the contribution of granules for crack self-healing process.

5.9 Chapter summary

In this chapter the development of granules with reserved hydration potential and their possible use as self-healing sand substitutions has been discussed. Meta (2018) indicated that the addition of coating liquid to mortar mixtures has a cement hydration reaction retarding effect there by resulting in disruption in mechanical strength development if used in large amount. This understanding has inspired the trials presented in this chapter to design cement granules with reserved hydration potential.

This granulation approach is considered to be advantageous over the former (PCA) approach as there would be no crushing for manufacturing the additives, hence, avoiding an expensive and an energy consuming process. Such types of cement granules are developed by making a balance between the ratio of total liquid (water + coating liquid) to cementitious powder and the ratio of coating liquid to water. Two types of cementitious powders; ordinary Portland cement and silica fume, were agglomerated in mortar mixer with a mixture of the coating liquid and water to manufacture granules with reserved hydration potential.

TG-DTA results confirmed that the inclusion of these granules in mortar samples show lesser degree of hydration compared to control samples which do not contain the granules. The addition of these cement granules resulted in water flow reduction reaching up to 85% for 28 days old samples and up to 70% for 91 days old samples of the test for an average crack width of 0.2 mm. From the results of the experimental study, it was inferred that the granule dosage rate continues to be important influencing factor for crack closure even at later ages for large crack widths of 0.3 mm or higher. Additionally, for larger crack widths of 0.3 mm and greater, further research is suggested to improve the performance of granules or even consider other possible crack width limiting techniques. .

At initial manufacturing stage the cement particles are agglomerated by a mixture of water and coating liquid using mortar mixer. The cement particles are expected to be bonded by thin layer of hydration products and small amount of the liquid mixture will be surrounding the granules. And this state is expected to continue after mixing for the first few weeks. As the time progresses the water contained in the granules will be gradually consumed for the hydration process of the cement particles while the non-reactive coating liquid remains surrounding the cement agglomerates and protecting their hydration by the contact of the mixing water. However, the full potential hydration of the granules is not expected to take place since the cement particles inside them will be partially covered and protected by the coating liquid until crack happens and they come in contact with water. The coating liquid is expected to protect the granules from direct contact with the concrete mixing water. Once crack occurs and water flow takes place, the coating liquid will get washed out by the action of running water and further rehydration of the granules is expected to bring about crack closure.

For further research it is highly recommended that the use of granules should be combined with crack width limiting techniques such as inclusion of fibers to bring about better self-healing performance in concrete. In addition, to achieve full crack closure not only OPC and SF but also other material combinations such as expansive and swelling agents as recommended by Ahn (2007) might help to reach the target. In this study the ratio of coating liquid to water was adopted to be 1:1. However, in the future higher ratios of the coating liquid could help in better reserving the hydration potential of granules while being applied with low w/c concrete mix designs.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this study, in appreciation of the efforts of other researchers to realizing the improvement of self-healing concrete by incorporating cementitious components, two new approaches are investigated. Although much remains to be done in achieving a complete crack closure with in short duaration of time, it was possible to have promising water flow reduction results by encorporating granules made with coating liquid. Based on the results obtained in tthe experimental study the following conclusions are drawn:

As first suggested approach Powder Compacted Aggregates (PCA) were prepared by compacting the cementitious and sludge powder mixtures inside a cylindrical mold using universal testing machine and crushing the resulting compacts by jaw crusher. After conducting water pass tests, it was shown that inclusion of the PCA contributes to water flow reduction. However, the performance of the samples incorporating PCA was not found out to be satisfactory given relatively young specimen of age 28 days were used for the experimental study. In addition, at the chosen formation pressures for the compacts the strength of the compacts themselves was very weak for the PCA to survive the mixing process of the mortar. Hence, the performance of the PCA could not be any advantageous over powder type self-healing additives (binary mixtures) with similar material compositions.

The second approach was the use of cement granules with reserved hydration potential. This approach is considered to be advantageous over the former (PCA) approach as there would be no crushing for manufacturing the additives, hence, avoiding an expensive and an energy consuming process. Such types of cement granules are developed by making a balance between the ratio of total liquid to powder and the ratio of coating liquid to water. Two types of cementitious powders; ordinary Portland cement and silica fume, were agglomerated in mortar mixer with a mixture of the coating liquid and water to manufacture granules with reserved hydration potential.

In general, the self-healing mortar samples showed higher flow reduction at the age of 14th, 28th and 56th day of the water pass test compared to the control sample for crack width of 0.2 mm.

Comparing the effect of granule type the effect of the difference in material composition between Type I (OPC case) and Type II (OPC+SF case) was not clearly visible until the 28^{th} day of water pass test. At long term tests of 56^{th} day, however, inclusion of the Type II granules brought about nearly zero water flow reduction likely due to the continuation of pozzolanic reaction of the Silica fume. Comparing the dosage rates of granules, marked differences in flow reduction are not exhibited when the dosage increased to from 60 kg/m^3 to 120 Kg/m^3 for the same granule type . At this stage the up to a maximum of 85 % water flow reduction was achieved at the end of the 28^{th} day of the water pass test for 28 days old samples with crack width of 0.2 mm.

Microscopic observations have shown that the control sample had relatively smaller size and widely dispersed crystals on the surface while self-healing mortar made by granules with reserved hydration potential had denser and larger sized products. Larger crystal sizes for self-healing mortar made by using coating liquid have been similarly reported by Meta (2018). The relatively better flow reduction is, thus, associated with more product formation exhibited by samples incorporating granules with reserved hydration potential.

It is inferred that the granule dosage rate becomes important influencing factor for crack closure at such large crack widths of 0.3 mm or higher. According to the results, almost all self-healing specimen with the higher granule dosage performed better in reducing the water flow compared to their respective samples with lower granule dosage. It is inferred that the granule dosage rate becomes important influencing factor for crack closure at such large crack widths of 0.3 mm or higher. At the applied dosage rates of 60 and 120 Kg/m^3, however, crack width of 0.3 mm was a severe case to reach full crack closure.

At the end of the 14^{th} and 28^{th} days of the water pass test, secondary vacuum soaking was introduced in this study following the same procedures as the initial one, to exclude effect of invisible air bubbles on the measured water flow and to verify the flow reduction resulting from solid precipitation and deposition only. Initially all the samples exhibited high water flow reduction, after the second stage vacuuming it was revealed that samples with self-healing additives show better flow reduction compared to the control. In reality crack closure is considered to be the phenomenon resulting from both solid deposition, hydration product formation, crystallization of minerals

6.2 Recommendations

In this study it was necessary to minimize the natural self-healing process by adopting higher water to cement ratio of 0.5 and to examine the contribution of self-healing for crack self-healing process. According to the results, the TG-DTA tests confirmed the control sample to show relatively higher degree of hydration than the self-healing mortar prepared with the granules. A difference of approximately 7% is calculated for mortar containing II_0.20 granules while the minimum difference in hydration degree, approximately 2%, was observed for mortars made with II_0.20. Over all hydration degree at this stage is very high (greater than 80%) for all samples since the water to cement ratio adopted for the mixes is 0.5. In reality, however, better reservation of hydration degree could be achieved with designing mixes with low water to cement ratios. In low water to cement ratio concrete mixes the cement matrix will contain large amount of unhydratred cement which contribute to the natural self-healing process when crack occurs.

For further research it is highly recommended that the use of granules should be combined with crack width limiting techniques such as inclusion of fibers to bring about better self-healing performance in concrete. In addition, to achieve full crack closure not only OPC and SF but also other material combinations such as expansive and swelling agents as recommended by Ahn (2007) might help to reach the target. In this study, the ratio of coating liquid to water was adopted to be 1:1. However, in the future higher ratios of the coating liquid could help in better reserving the hydration potential of granules while being applied with low w/c concrete mix designs. In addition, where cost is not a priority, for instance for toxic waste tanks, higher dosage of granules might be used as extreme measure to make self-healing concrete.

It is hoped that the progress and results of this study have highlighted the possible improvement of to crack healing ability by reserving initial hydration reactivity of cementitious additives. It is highly recommended that further research be conducted with several material combinations and several type of coating liquids to achieve full crack closure and the extent of this possibility. In addition, long term self-healing capability of including granules prepared by using coating liquid needs to be studied.

REFERENCES

[1] Hirozo Mihashi & Tomoya Nishiwaki (2012), “Development of Engineered Self-Healing and Self-Repairing Concrete-State-of-the-Art-Report,” Journal of Advanced Technology, Vol. 10, pp. 170-184, 2012

[2] Breugel, K. V., “Is there a market for self-healing cement-based materials?” Proceedings of the 1st International Conference on Self-Healing Materials, Delft, Netherlands, 18-20 April 2007.

[3] E. Schlangen and S. Sangadji, “Addressing infrastructure durability and sustainability by self-healing mechanisms—recent advances in self-healing concrete and asphalt,” Procedia Engineering, vol. 54, pp. 39–57, 2013.

[4] Tae-Ho Ahn & Toshiharu Kishi, “Crack self-healing behavior of cementitious composites incorporating various mineral admixtures,” Journal of Advanced Concrete Technology, Vol. 8, May 2010, pp. 171-186.

[5] .De Rooij, M.; Van Tittelboom, K. & De Belie, N., Schlangen, E. “Self-Healing Phenomena in Cement-Based Materials,” State-of-the-Art Report of RILEM Technical Committee 221-SHC, Self-Healing Phenomena in Cement-Based Materials: Springer, Dordrecht, the Netherlands, 2013.

[6] NL Agency, Dutch Ministry of Economic Affairs, “Self healing materials concept and applications,” Second edition - Version 2013, May 2013.

[7] Kim Van Tittelboom & Nele De Belie, “Self-Healing in Cementitious Materials – A Review,” Journal of Materials, Vol. 6, pp. 2182-2217, 2013.

[8] Shin-ichi Igarashi, Minoru Kuneda & Tomoya Nishiwaki, Japan concrete Institute, Technical Committee Reports – Digest Edition, Technical Committee on Autogenous Healing in Cementitious Materials, JCI-TC075B, 2009.

[9] De Rooij, M.; Van Tittelboom, K.; De Belie, N.; Schlangen, E. Self-Healing Phenomena in Cement-Based Materials, State-of-the-Art Report of RILEM Technical Committee 221-SHC: Self-Healing Phenomena in Cement-Based Materials; Springer: Dordrecht, the Netherlands, 2013.

[10] M. Wu, B. Johannesson, M. Geiker, “A review: Self-healing in cementitious materials and engineered cementitious composite as a self-healing material”, Journal of Construction and Building Materials, Vol. 28, pp. 571–583, 2012.

[11] Amirreza Talaiekhozan, Ali Keyvanfar, Arezo Shafaghat, Ramin Andalib, M.Z Abd Majid, Mohamad Ali Fulazzaky, Rosli Mohamad Zin, Chew Tin Lee, Mohd Warid Hussin, Norhaliza Hamzah, Nur Fatimah Marwar & H.I. Haidar, “A review of Self-healing in Concrete Research Development”, Journal of Environmental Treatment Techniques, Vol. 28, pp. 1-11, 2014.

[12] Van Tittelboom, K.; de Belie, N.; van Loo, D.; Jacobs, P. Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent, Journal of Cement and Concrete Composites, , Vol. 33, pp. 497–505 2011.

[13] C. Edvardsen, “Water permeability and autogenous healing of cracks in concrete,” ACI Mater

J, Vol. 96, pp.448–54, 1999.
[14] A. Neville, “Autogenous Healing Concrete Miracle, Concrete International,” Vol. 24(11), pp.76-82, 2002.
[15] V. C. Li, & E.Yang, Self healing in concrete materials. In S. van der Zwaag (ed.) (2007) Self healing materials – An alternative approach to 20 centuries of materials science. Springer, The Netherlands, pp.161–194.
[16] Vu Viet Hung, Performance Improvement of Self-healing Concrete by Development of Semi-Capsulation Technique for Functional Effective Ingredients, Ph.D. dissertation, August 2013, The University of Tokyo.
[17] Hearn N, Morley CT., “Self-healing, autogenous healing and continued hydration: what is the difference?” Mater Struct, 1998; Vol. 31, 563–567.
[18] Daisuke Sawaki & Etsuo Sakai, “Characterization for Long-aged Hardened Cement Collected from Old Structures by Modern Technique Chemical Analysis,” Journal of Advanced Concrete Technology, Vol. 5(3), September 2007, pp. 325–331.
[19] Toshiharu Kishi, “Development of Crack Self-healing Concrete by Cost Beneficial Semi-Capsulation Technique,” In: Proc. The Third International conference on Sustainable Construction Materials and Technologies, August 2013.
[20] Nasiru Zakari Muhammad, Arezou Shafaghat, Ali Keyvanfar, Muhd Zaimi Abd. Majid, S.K. Ghoshal, Seyed Esmaeil Mohammadyan Yasouj, Abideen Adekunle Ganiyu, Mostafa Samadi Kouchaksaraei, Hesam Kamyab, Mohammad Mahdi Taheri, Mostafa Rezazadeh Shirdar, Ronald McCaffer, “Tests and methods of evaluating the self-healing efficiency of concrete: A review,” Journal of Construction and Building Materials, Vol.112, pp. 1123–1132, 2016.
[21] K. Van Tittelboom, D. Snoeck, J. Wang and N. De Belie, “Most recent advances in the field of self-healing cementitious materials,” in proc. ICSHM 2013, pp. 406-413, 2013.
[22] Abd-Elmoaty, A.-E., “Self-healing of polymer modified concrete,” Alex. Eng. J., 2011, Vol. 50, pp. 171–178.
[23] http://www.cement.org/cement-concrete-applications/concrete-materials/supplementary-cementing-materials, accessed on July 11, 2018.
[24] Pipat Termkhajornkit, Toyoharu Nawa, Yoichi Yamashiro & Toshiki Saito, “Self-healing ability of fly ash–cement systems,” Journal of Cement & Concrete Composites Vol. 31, pp. 195–203, 2009.
[25] “Cement and Concrete Terminology,” SP-19, American Concrete Institute, Detroit, Michigan, pp. 107, 1988.
[26] G. Baert, “Physico-chemical interactions in Portland cement (high volume) Fly ash binders”, Ph.D. dissertation, Ghent university, 2009.
[27] Y. Ishikawa, “Basic research on the self-healing functions of concrete mixed with fly ash,” In proc. ICSHM2013, pp. 248-252, 2013.
[28] Haoliang Huang, Guang Ye & Denis Damidot, Effect of blast furnace slag on self-healing of micro cracks in cementitious materials, Journal of Cement and Concrete Research, Vol. 60, pp. 68-82, 2014.

[29] RA. B. Depaa and T. Felix Kala, "Experimental Investigation of Self-Healing Behavior of Concrete using Silica Fume and GGBFS as Mineral Admixtures," Indian Journal of Science and Technology, Vol 8(36), 2015.
[30] Toshiharu Kishi, Tae-Ho Ahn, Akira Hosoda, Shoko Suzuki & Hiedaki Takaoka, "Self-healing behavior by cementitious recrystallization of cracked concrete incorporating expansive agent," In proc. The first international conference on self-healing materials, Noordwijk aan Zee, The Netherlands, 2007.
[31] K. Sisomphon, O. Copuroglu, E.A.B Koenders, "Self-healing of surface cracks in mortars with expansive additive," Journal of Cement and Concrete Additives, Vol. 34, pp. 566-574, 2012.
[32] S. Nagataki, H. Gomi, Expansive admixtures (mainly ettringite), Journal of Cement and Concrete Composite, Vol. 20, pp. 163–170, 1998.
[33] Tao-Ho Ahn, Development of Self-healing Concrete Incorporating Geo-Materials: A study on its Mechanism and Behavior in Cracked Concrete, Ph.D. dissertation, 2007, The University of Tokyo.
[34] V. V. Hung, T. Kishi & T.H. Ahn, Development of Self-healing Granules Having Semi-Capsulation effect by Using Cement Compound, Chemical Admixtures and its Water Tight Performance through Crack, In: Proc. International Conference on Self-healing Materials, 2013, pp. 418-421.
[35] H. Ikoma, T. Kishi, Y. Sakai & M. Kayondo, Elucidation of Rapid Reduction of Water Flow through Concrete Crack Regarded as Self-Healing Phenomenon, International Conference on Self-healing Materials, 2015, Abstract ID No.: 75
[36] M. Kayondo, S. Sato & T. Kishi, Detailed Observation of Air Bubble Generation by Water Flow Hydrodynamics in Narrow Gaps such as Concrete, International Conference on Self-healing Materials, 2015, Abstract ID No.: 74
[37] Muzafalu Kayondo & Toshiharu Kishi, "Water Flow Reduction and Air Bubble Generation Mechanisms in Narrow Interfaces such as Concrete Cracks," In: Proc. Japan Concrete Institute, 2016, Vol. 38(1), pp. 1671-1676.
[38] Kayondo Muzafalu, Experimental Study on the Effect of the Air – Water Interface Created at Wall Surface on Water Flow in Narrow Gaps, January 2017, Ph.D. dissertation, The University of Tokyo.
[39] Michael E. Aulton & Kevin M. G. Taylor (2013) Aulton's pharmaceutics: The design and manufacture of medicenes. London, Churchill Livingstone Elsevier.
[40] G.S.Upadhyaya (2002) "Powder metallurgy technology", Cambridge International Science Publishing, England.
[41] D. Bika, G.I. Tardos, S. Panmai, L. Farber and J. Michaels (2005)."Strength and morphology of solid bridges in dry granules of pharmaceutical powders," Journal of Powder Technology, 2016, Vol. 150, pp.104–116.
[42] I. Soroka & Peter J. Sereda (1970). The structure of cement stone and the use of compacts as structural models. National research council of canada , pp. 67-73.

[43] R.F. Feldman and P.J. Sereda (1970), "A new model for hydrated Portland cement and its practical implications," National research council of Canada, Division of Building research, Paper no. 454.
[44] Yuya Sakai, Tarekegne Biruktawit Taye and Toshiharu Kishi (2014), "Complete recycle of waste concrete by compaction," In: Proc. International conference on the regeneration and conservation of concrete structures, Nagasaki, Japan.
[45] Wolfgang Pietsch, "Size enlargement by agglomeration : A hand book of powder science and technology" John Wiley & Sons/Salle + Sauerländer, Chichester, UK/Aarau, Switzerland (1991), pp.202-307,
[46] Tep Meta, "Study on Application of Heated Sludge Powder and Coating Liquid to Crack Self-Healing Mortar," Master's thesis, February 2018,The University of Tokyo.

ANNEX

Table A.1 Mix proportions of PCA prepared for preliminary tests

PCA designation	Formation pressure (MPa)	Mix proportion by weight (%)			
		Sludge powder	OPC	FA	BFS
OPC 10	10	50	50		
OPC 25	25				
FA 25	25			50	
FA 50	50				
BFS 25	25				50
BFS 50	50				

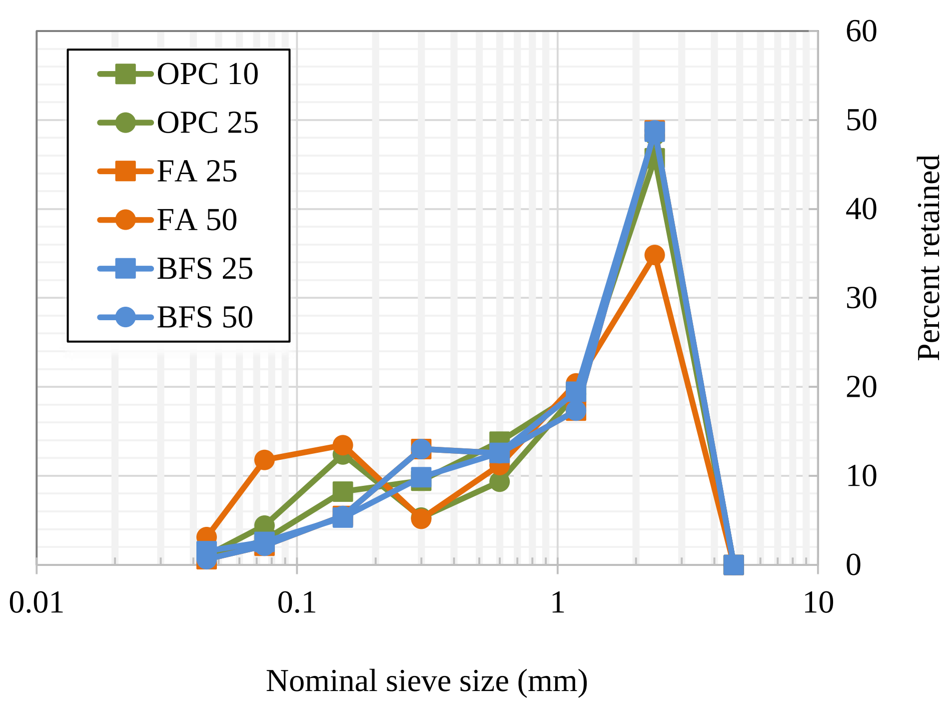


Figure A.1 Gradation of the PCA prepared for the preliminary tests

Table A.2 Mix proportion of mortar for preliminary test

w/c	**Unit weight (Kg/m^3)**				**Designation**	**Notes on curing**
	Water	**Cement**	**Sand**	**PCA**		
0.5	264	528	1345	0	Control	Water curing for 28 days
			1285	60	(60)	
			1225	120	(120)	

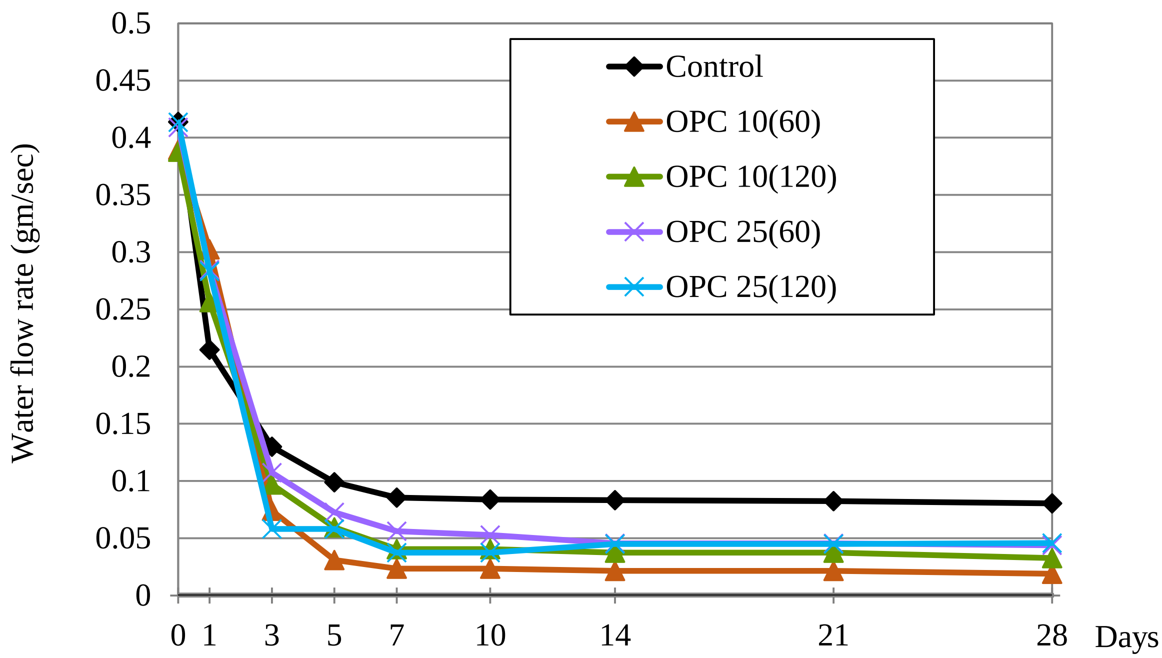


Figure A.2 Mortar water flow test results for OPC type PCA

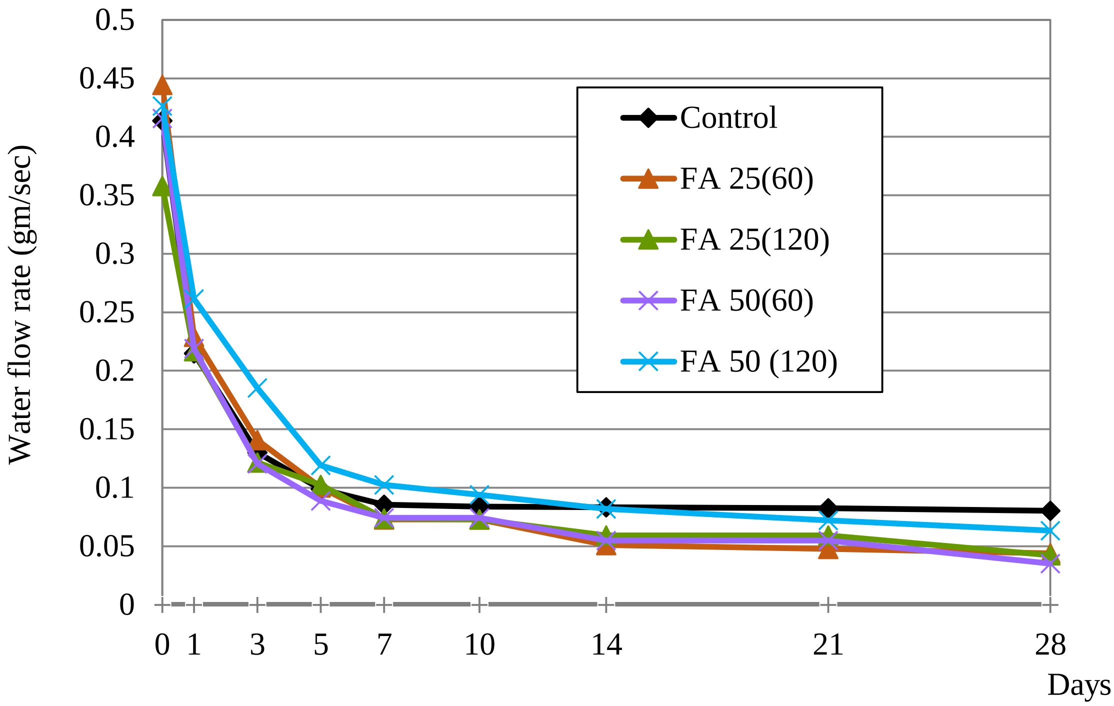


Figure A.3 Mortar water flow test results for FA type PCA

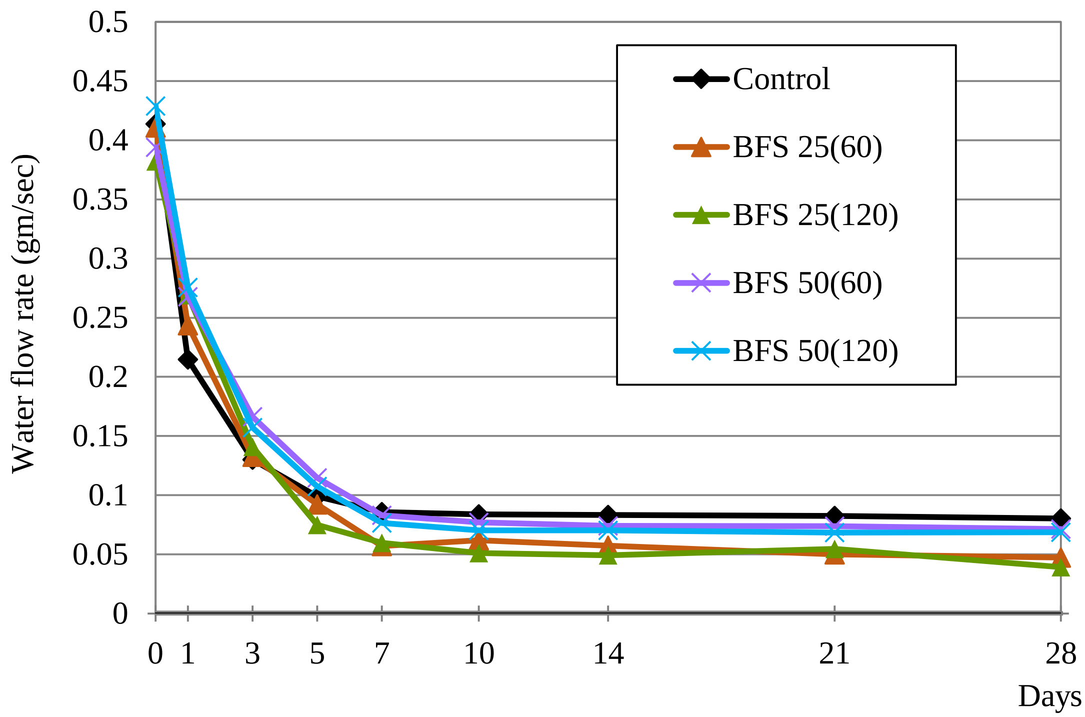


Figure A.4 Mortar water flow test results for BFS type PCA

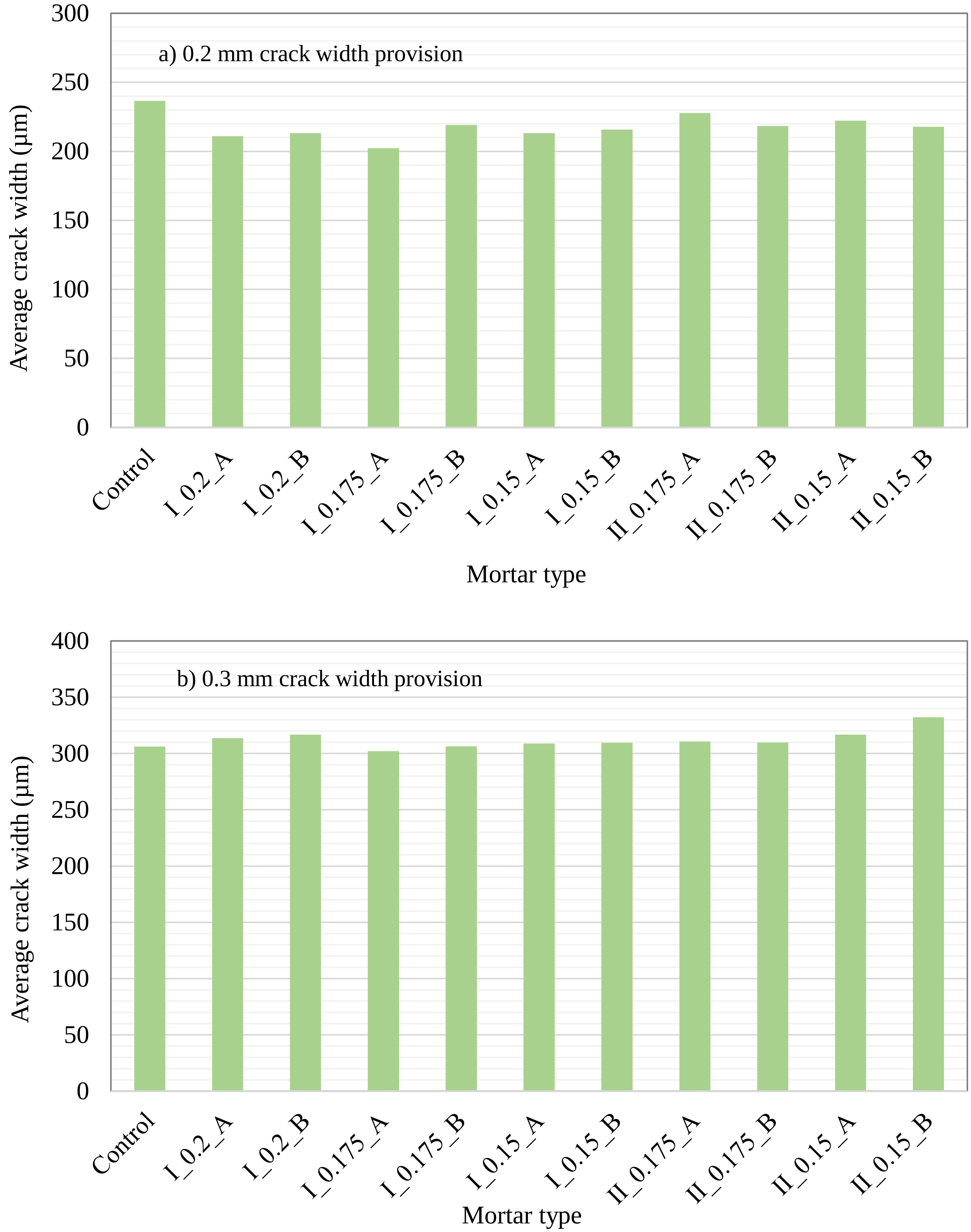


Figure A.5 Average crack width measurements for 28 days old samples (a) 0.2 mm crack width (b) 0.3 mm crack width provision

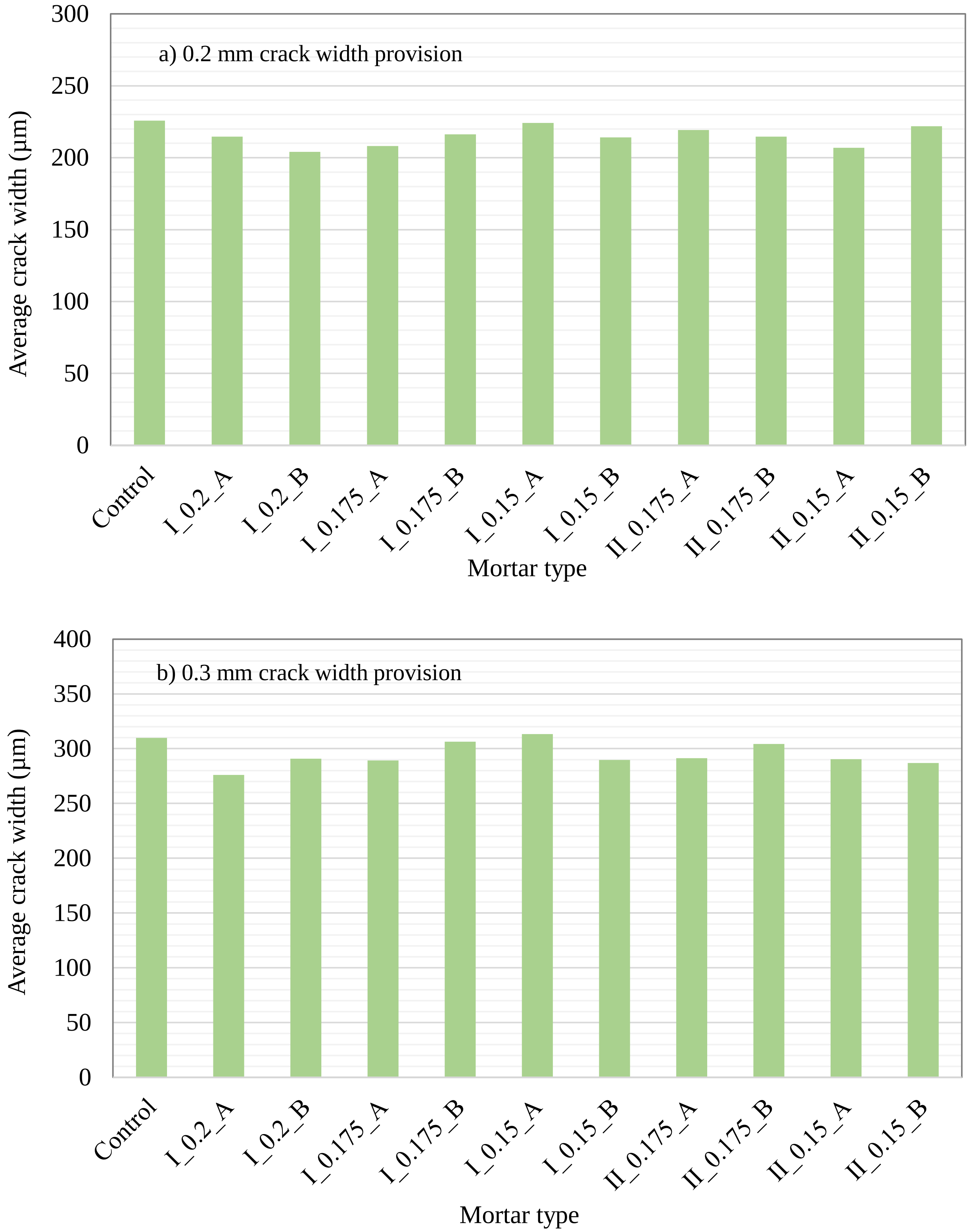


Figure A.6 Average crack width measurements for 28 days old samples (a) 0.2 mm crack width (b) 0.3 mm crack width provision