Experimental study on the effect of the air - water interface created at wall surface on water flow in narrow gaps.

(壁面に形成された気液界面が狭小空間中の水の流れに与える影響
に関する実験的検討)

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Abstract

Water flow in narrow gaps characterized by porous surfaces has been observed to breed air bubbles that stay strongly fixed on the surface of water flow. Water flow in porous media or between parallel plates is well understood, through equations and simulations. However, there have been some limitations to this understanding, based on the findings of this research and some previous research. Flow between parallel plates or porous media attempts to cater to the varied material characteristics such as material roughness by incorporating a material factor. In reality, and especially for narrow gaps of water flow, the surface over which water flows could be modified due to the interaction between water and the surface over which it flows. Therefore, water seizes to flow directly over the surface in such a case. By this research, the flow surface could be enveloped by air bubbles, and the properties of the surface would then become completely different from those previously envisaged. A new surface, whose overall area could now be more than that of the primary material, now, determines the properties of flow.

Unlike in closed interfaces, a direct water flow observation technique has been adopted to simulate actual water flow in narrow gaps. A transparent glass panel bound to a study material, while leaving a narrow gap between the two, is used as a set-up to observe water flow directly. This set-up is connected to a continuous water supply container, and resembles the set-up of the water pass test for crack self-healing concrete. With this kind of specimen set-up, and other aids such as good lighting, and video recording, a lot of data can be collected about water flow. The flow rate can be measured, and visual observations made.

In self – healing concrete testing, this observed effect of air bubbles creation and growth could be mistaken for actual self-healing products deposition within crack interstices. This is because it mimics the actual water flow reduction effect due other well-known mechanisms of self – healing concrete. In this research, the contributory effect of air bubbles in the initials stages of water supply during self – healing testing concrete has been clarified. The mechanisms of air bubble growth too have been investigated. The

effect of water supersaturation, presence of nucleation points on the water flow surface, plus continuous water flow are necessary conditions for air bubble growth. Minus any of these, bubble growth becomes stagnated. These mechanisms however, are only of an accelerating role for air exchange at the air – water interface. Different materials possess different surface characteristics and thus different potential for the air bubble effects and water flow, when bound in narrow gaps of water flow. In this research, concrete, pumice, wood, glass, Styrofoam, aluminium, plastics have been investigated and compared for their ability to cause air bubbles contribute to water flow reduction mechanisms when bound in narrow gaps.

Water flow over a solid surface experiences drag resistance due to the non-slip boundary condition. Micro air bubbles have been used in several applications to reduce surface friction, for example in ship propulsion. In the cases where this is utilized, the air bubbles are not fixed on any surface; they are released near the surface that experiences drag. In this research however, consideration is made for micro and nano air bubbles that are created and fixed at the surface of water flow within narrow gaps. Here, the bubbles do not serve to reduce flow drag (from the results and observations of this research). Once the air bubbles are hinged, or fixed on a surface of water flow, their effect becomes quite apparent. In narrow interfaces, the water flow braking effect of surface anchored micro and nano air bubbles is well pronounced based on the findings of this research. It has been found that this effect is capable of reducing water flows by an average of about 15%. If the water is air – rich, and the micro and nano bubbles have been formed, they have the potential to grow into large millimeter size air cavities. These would then further block water flow and contribute to further water flow reduction. At this point, flow could be constricted by more than 60% depending on the ambient conditions, gap size, and other flow parameters.

The effect of large air bubbles blocking water flow was largely understood in related research, and initially thought to be the main cause of water flow reduction. However, with continuous observations, and within smaller time intervals of water flow measurements, it was observed that water flow reduction continues to take place even in the absence of large millimeter size air bubbles. The water flow reduction in this case is due to micro and nano air bubbles that are fixed or anchored at the wall surface of water flow as could be observed by a microscope. The mechanism of water flow reduction by these surface anchored micro and nano air bubbles is by water flow braking by the fixed air – water interface. In this research, a hypothesis about the nature of the water surface is proposed. Although current knowledge of the air – water

surface is largely understood in terms of surface tension (surface energy), a microscopic clarification of the behaviour of the air – water interface is necessary. It is further hypothesized in this research that water molecules at the air – water interface adopt a fixed arrangement in which molecular rotation is restrained. This fixed and structured molecular layer interacts with both the freely flowing bulk water molecules on one side, and the freely moving air molecules on the opposite side. The zone of influence of this restrained water layer gradually extends only into the bulk liquid. In this research, this fixed molecular layer plays a role in dampening water flow in narrow channels. Away from the interface and into the bulk, water molecular rotation is gradually allowed, and flow (rotation) speed becomes faster. In relatively large channels, the effect of this mechanism is almost negligible, but cannot be underlooked in smaller interfaces.

In order to strengthen this theory, an experimental approach has been adopted still utilizing the visual observation technique. In this experiment, an air – water interface is created, in a relatively narrow gap (about 2 – 3 mm), and observations are made at this interface. Unlike most water interfacial research, where a static liquid layer is studied, in this study, the interface created between air and moving water is studied to reflect the perspective of this research. Air is trapped in a bubble within a narrow gap, creating an air phase over which water continuously flows. The vibration of the interface; dampening of a spinning floatable sphere connected to an air bubble with the flow path; persistent adsorption and retention of luminescent molecules at the interface despite continuous water flow (only observable in UV-light); and the conveyance of luminescent molecules by rising air bubbles, all help to reinforce the said hypothesis, as observed in this experimental approach. With this understanding and hypothesis, several of the dominant mechanisms or observed phenomena involving water flow through narrow gaps could be explained.

The nature of the air – water interface is still complicated, and several researchers are attempting to better understand its behaviour in order to find areas of application and also to propel science forward. In concrete technology for example, where water permeation through the dense micro pore structure determines material durability, understanding these water flow mechanisms is important in finding lasting solutions for our infrastructure. It is hoped that this research could help shed more light on several water ingress related mechanisms at a smaller scale of focus.

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Chapter 1 Introduction

1.1 General

Water flow has been greatly studied in the general field of science and for larger dimensions of emphasis. In the last century and present, a new dimension of science has brought in question the behaviour of mechanisms and processes at the smallest scales. With the observation of microscopic behaviours, a new era of understanding of the uniqueness of materials and the possible manipulation of their properties is brought into focus. Water flow too is intriguing, especially the one that takes places in narrow gaps! Of course, the nature of water, its uniqueness, and the cause of its diverse properties is not well understood even today. However, for the progress of science, a clear and concise understanding of the fundamental behaviour of water in its various states and conditions needs to be established. Without doing this, we can't explore the several interconnected processes that involve not only one state, but multiple phases of water.

In the bulk, water flow is clearly understood. In narrow gaps however, observations reveal different results, which points to the existence of unique mechanisms or behaviors unnoticeable in the bulk scenarios. This research attempts to explore previously insinuated water flow uniqueness in narrow interfaces. It is initially based on the premise of air bubbles being created in the path of water flow. This was observed to cause significant water flow reduction, as would be expected, because of their water flow blocking effect. Further experimentation revealed that, even in the absence of the blocking effect, air bubbles could still cause notable water flow reduction, through their water flow braking effect. It is the water flow braking effect mechanism that points further to water's unique behaviour in narrow gaps such as concrete cracks. This research points to the air – water interface of micro and nano bubbles as the cause of water flow braking. But how does the air – water interface generate such an effect? A hypothesis of how this happens has been proposed, and it clarifies on our current understanding of the surface tension of water, and the nature of the air – water interface.

In general, surface tension is expressed in terms of surface energy, and there lacks a microscopic understanding of the actual behaviour during water flow, or at multiple interfaces. In the bulk, the effect of surface tension can be ignored; but when it comes to micro, nano, or smaller dimensions, the effects can no longer be ignored. The question at point in trying to understand how this happens can no longer be answered based on our traditional understanding of surface energy. A molecular perspective could perhaps

shed more light on the mechanisms involved. This is the attempt of this research. This research however extends beyond understanding water in concrete cracks, to micro fluidic devices, and biological systems involving fluid flow.

1.2 Background

There are several attempts to come up with well researched and engineered materials, especially given the current challenges our infrastructures face today. In concrete structures, the main worry has always been the slow deterioration that occurs, cutting short the expected lifespan of these structures. This kind of slow cancer can either originate from inside or outside the concrete. Challenges from outside the structure are mainly ingress of water plus its associated deleterious constituents [1], [2]. It's these that create havoc and speed up the deterioration of a material that is expected to last hundreds of years. Concrete cracks for example provide a faster route for water ingress or leakage. Self-healing concrete is in developmental stages for this purpose mainly – to quickly provide a blocking mechanism to water permeation, or better, enable the structure regain its earlier structural soundness, or perform as intended [3], [4], [5] [6].

As much as there have been seemingly interesting approaches thus far, there are some challenges that need to be addressed. Self-healing testing that involves water permeation into concrete or through a static penetrating crack with water flow, may be flawed. Recent findings [7] point to the creation of large air bubbles that block water flow, simulating results of traditionally known mechanisms of self – healing. Figure 1-1 illustrates the typical results of water flow through a straight crack, water flow reduction occurs without any visible healing products, but instead visible air cavities could be seen.

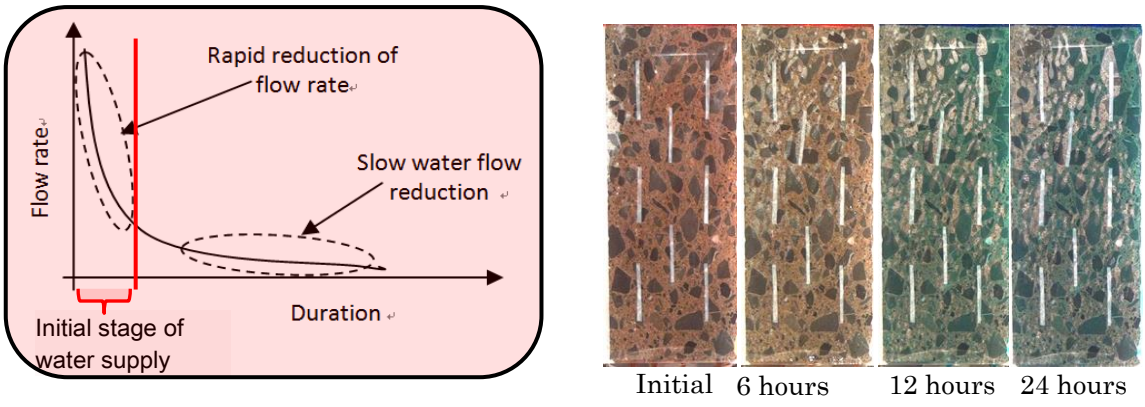

Figure 1.1: Rapid water flow reduction, associated with creation and growth of air bubbles in crack gaps.

This research stems from this observation [7] (Figure 1-1 right), and goes on to challenge the traditionally well understood equations of water flow, such as the Hagen Poiseuille, Darcy and the Washburn equations [8], [9]. How well do these equations actually represent water flow in porous media or parallel surfaces? Or how well do they represent the interaction between water and the surfaces over which water flows. These equations do not sufficiently explain the discrepancy in water flows due to creation of air bubbles, especially for flow in narrow gaps. Figure 1-2 shows effluent flow rate for different supersaturation levels at water treatment plant, with the differences attributed to supersaturated water's potential to cause air bubbles. The contributory effect of air bubbles on water flow and their growth mechanisms have been extensively studied in a part of this research [10]. By adopting a visual observation technique of water flow, air bubble growth can be observed and water flow changes measured extensively [11]

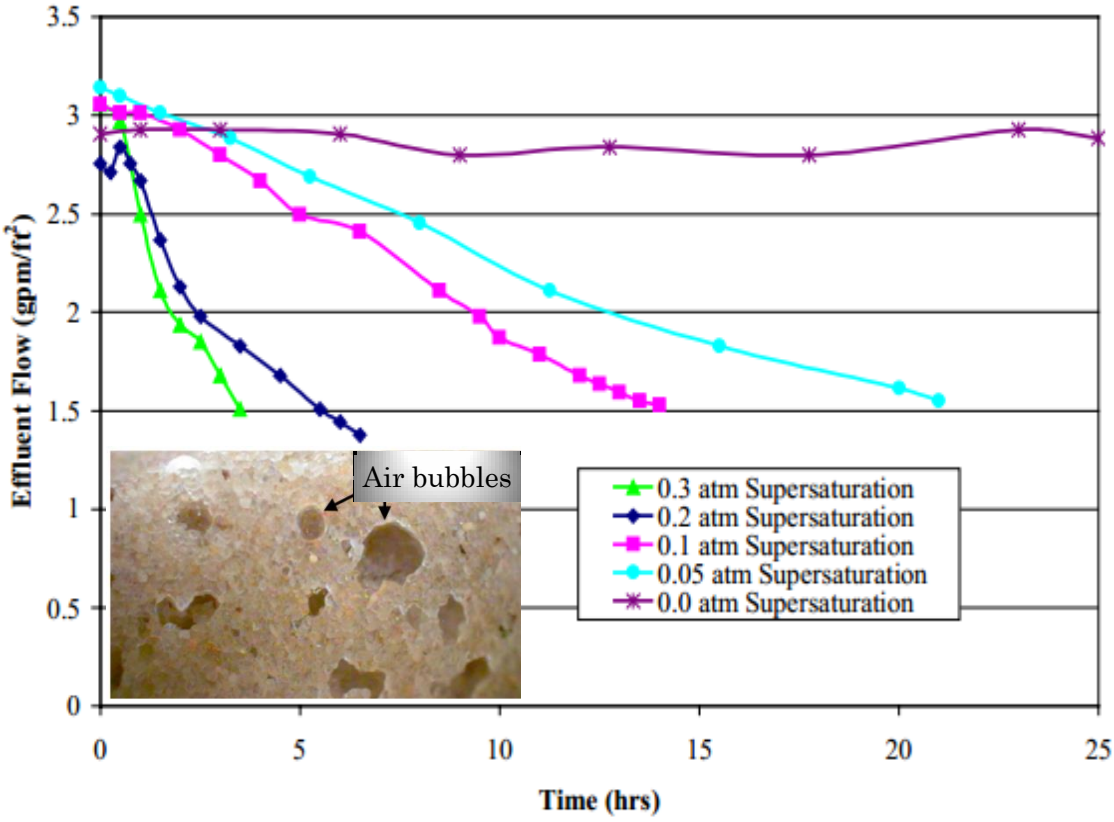

Figure 1-2: Effect of supersaturated water on effluent outflow at water treatment plant that utilizes sand media for water treatment (Scardina and Edwards, 2004)

Beyond the blocking effect of large air bubbles, micro and nano air bubbles also have a braking effect on water flow. The mechanisms of water flow braking by nano and micro

air bubbles is due to the nature of the air – water interface [12].

The air – water interface once created, is lined by water molecules. The behaviours and tendencies of this surface are largely understood via the current thermodynamic perspective of surface tension [13], [14], [15], [16], [17] which is not clear about the molecular behavior (rotation or fixation) or even position stability at the interface. In this research however, it is hypothesized that these interfacial molecules assume a fixed arrangement with minimal position rotation. They are then not as freely moving as their bulk counterparts; and this is the main cause of water flow braking as the bulk molecules race past the fixed surface layer [12]. There are a considerable number of researchers attempting to clearly explain the discrepancies that exist at the air – water interface [13], [18], [19], but current findings are inconclusive on its exact nature.

Experiments about the air – water interface for a condition where continuous water flow occurs have been performed probably for the first time in our research. Most researchers studying the water interface do so for isolated and static water surfaces. Since this research appeals to water flow in narrow gaps and the effect of interstitially formed air bubbles, it was necessary that the experimental investigation depicts actual phenomenon. Thus, in order to reinforce the hypothesis of this research, indirect approaches through experimentation have been done.

1. Initially, and through sheer observation of water flow over a static air bubble, a rippling and vibrating interface depicts resistance to flow.

2. Additionally, persistent fluorescent molecular adsorption at the interface can be observed under ultra violet radiation, even long after the molecular solution is added to the set-up.

3. The secondary molecular substitution of luminescent molecules adsorbed at the interface by surfactant molecules, proves that the luminescent molecules were initially held in a fixed position at the air – water interface.

4. Another experiment was designed based on buoyancy and the assumption of a fixed nature of the air – water interface. A spherical floatable ball was placed in a dent within two parallel surfaces. Once water is supplied, the ball should be able to spin as long as it is not in contact with any trapped and fixed air bubble. If the spinning ball gets in contact with the air – water interface, the spinning is quickly dampened and brought to rest. This further revealed the restrained rotational nature of air – water interfacial molecules.

In reality, and to the extent of most research until today, water is a unique substance. It possesses unusual properties, totally different from other substances with similar molecular masses [20]. The strong nature of its hydrogen bonds causes several anomalous properties such as high melting and boiling points, low compressibility, unusual solubility properties, and several other properties that cannot be explained clearly. Besides its inherent properties, water displays a lot of uniqueness in combination with other substances, and in different environments and conditions. Though largely studied, water in its three states (liquid, solid and gas) is still a strange substance. The nature of water's physical interaction with other states of matter is one of the emphases of this research. How it behaves while moving in narrow spaces, especially as a liquid, determines the performance of many micro systems in use today, both in the built world or the natural realm.

1.3 Purpose and scope of this research

This research has been done mainly to deepen the understanding of water flow mechanisms in narrow gaps such as concrete cracks. However, the scope of findings from this research would extend beyond concrete cracks to apply to water permeation through not only the concrete micro pore structure, but also in other porous media such as soils.

Additionally, this research clarifies on the mechanisms of air bubble formation in narrow gaps of water flow as has been recently observed during crack self-healing testing via the direct visual observation approach of water flow. These mechanisms of air bubble growth present an anomaly according to the theoretical understanding of air bubbles, and it was the goal of this research to explore their formation mechanism in thin interfaces.

This research also attempts to explore the nature of the air water interface exposed to water flow for those air bubbles that are fixed on the surface within the narrow gaps.

Thus, the scope of this research is limited to water flow in narrow gaps (0.1 – 0.2 mm) for experimental investigations mainly. It also focuses on air bubbles that are created at a fixed point within the path of water flow. Contrary to common understanding, these air bubbles persist within the path of water and achieve stability within the narrow gaps. Comparisons are made to traditionally known air bubble dynamics and their behaviour and effects in narrow gaps.

1.4 Main contributions of this research

This research has clarified on the mechanisms of water flow reduction in narrow gaps due to the effect of air bubbles growth. The mechanisms have been characterized into two: Water flow braking by air bubbles when they are still small and haven't covered the entire width of the gap; and water flow blocking due to fully grown and fixed air bubbles physically blocking water flow.

In order to explain the mechanism of water flow braking by finer air bubbles, this research has proposed a new hypothesis about the nature of the air – water interface of surface fixed air bubbles within narrow gaps having water flow. The hypothesis is that water molecules at the air – water interface assume a fixed molecular arrangement with restricted molecular rotation compared to other water molecules in the bulk liquid.

1.5 Outline of thesis

Chapter one introduces the general background of this research and lays a firm foundation for the later chapters

Chapter two describes the current understanding of crack self-healing concrete and its water permeation testing approach. The hydraulics involved is discussed here based on the characteristics of the cracks, existing literature and the findings of this research.

Chapter three highlights the recent observation of air bubble creation and growth within not only concrete cracks, but other narrow gaps of water flow. The experimental procedures, methods of analysis, plus the quantification of the effect of this phenomenon on water flow are discussed here, side by side with the relevant literature.

Chapter four discusses the anomaly of air bubble coexistence amidst water flow. The stability of fixed air bubbles in narrow gaps, their anchorage mechanisms, and the effects of different parameters such as water quality are discussed and analyzed.

Chapter five gives a detailed description of air bubble growth observations and necessary conditions for this growth. Other known causes of air bubble growth in existing literature are discussed, and compared with observations in this research.

Chapter six clarifies the new understanding of water flow reduction in narrow gaps of water flow based on experimental investigations.

Chapter seven highlights the influence of the air – water interface on water flow mechanisms in narrow gaps with surface fixed air bubbles. The surface tension is

critically analyzed, and a hypothesis on the nature of the air – water interface is proposed.

Chapter nine mentions the conclusions and contributions of this research, plus the necessary recommendations and future works.

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Chapter 2 Self-healing concrete and water flow

2.1 Self-healing theory and mechanisms in concrete

Self-healing concrete is probably looked at as the future of concrete technologies. The idea that a concrete structure can have the ability to heal any inherent cracks that develop from time to time is actually exciting for most structural and materials engineers. Self-healing concrete is expected to make concrete last longer than is currently able to. It achieves this by being able to repair any defects that develop within the concrete, especially cracks that would compromise the robustness of the concrete structures. Figure 2-1 shows crack closure due to different self-healing approaches available today [1].

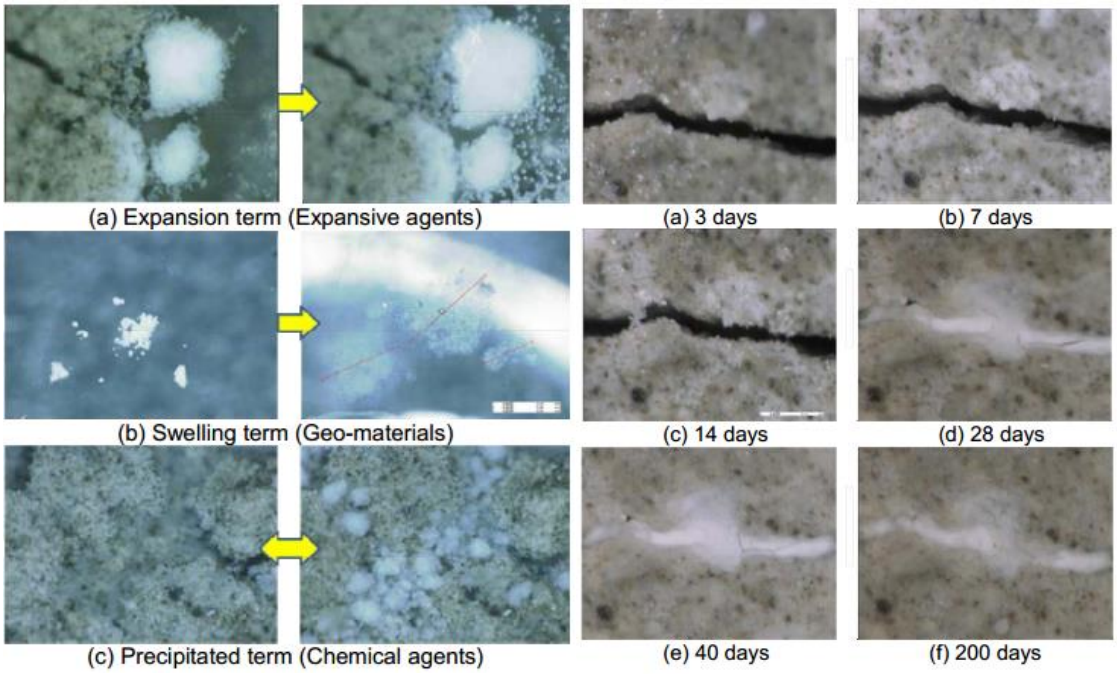

Figure 2-1: Design of composite materials with self-healing capability and Crack closing action (Ahn & Kishi, 2010) [1]

Though still in developmental stages, the challenges to come up with a working and reliable approach is still tricky. Too expensive and it won't be adopted, or too unreliable and users will lose faith in it! Most important of these two challenges at the moment, is to come up with a really versatile and reliable self-healing approach. In this regard, every aspect of the development stage needs to be considered; right from the healing materials used, to the testing methods.

One of the predominant testing methods involves passing water through a static

penetrating crack, and measuring water outflow rates with time. It is referred to as the water pass test. This method also uses water as a trigger for the several of the clearly understood mechanisms of self-healing, such as rehydration of unhydrated cement clinker, formation of calcium carbonate, expansion, and others. Many researchers have adopted the use of this simple method to attempt to deduce the extent of self-healing [2], [3], [4], [5], and [6].

2.1.1 Mechanisms of Self-healing

The concept of self-healing is not entirely a new discovery as it was already observed in old concrete structures more than a century ago in the form of white residues at crack points of retaining structures. Concrete in itself has some self-healing property that it owes mainly to partial cement hydration. However, this self-healing capability is limited to relatively small cracks (less than 100microm) and is termed autogeneous healing.

General concrete use in practice adopts mixtures with low water/cement ratio (0.45-0.55), and research has shown that such concrete retains about 20-30% of unhydrated cement which is said to contribute to autogeneous crack self-healing. Once the cracks occur and get exposed to water, anhydrous cement grains hydrate and the growth of hydration products contributes to crack closure for cracks that may penetrate the cement matrix.

Self-healing in cementitious materials is said to occur due to several of the following mechanisms as suggested by past researches (Ter Heide, 2005) [7] in Figure 2-2.

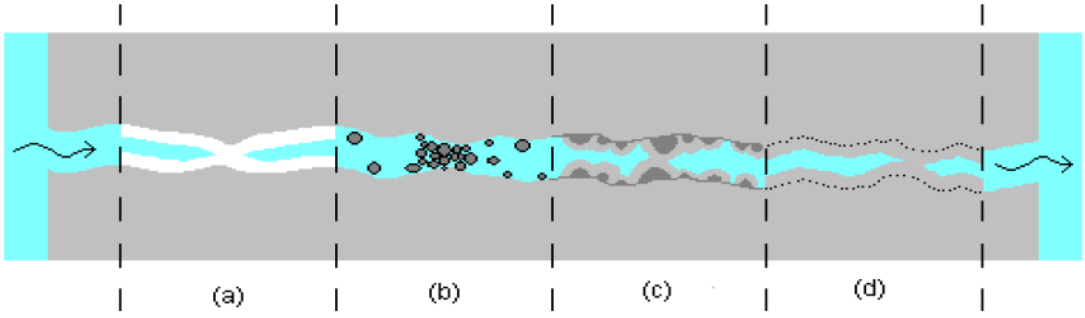

Figure 2-2: Self- healing mechanisms: a) dissolution, deposition and crystallization, b) Sedimentation, c) continuing hydration and d) swelling of the cement matrix.

Formation of Calcium carbonate or calcium hydroxide: Calcium is a basic ingredient of cementitious compounds and as such precipitates out in the presence of atmospheric carbon dioxide (Equation 1). The precipitated carbonate deposits on the crack surface and crack closure results.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad \text{..... (1)}$$

Sedimentation of particles within the crack interstices: On cracking, concrete produce smaller constituent particles that may be moved along with flowing water. These, combined with the impurities in flowing water may cause sedimentation and block flow of water contributing to self-healing.

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

Continued hydration: Cement hydration persist for quite a long period of time depending on the availability of water in the cement matrix. On cracking, unhydrated cement particles may be exposed to water and their formed hydrated products may fill up the cracks causing crack closure.

2.1.2 Verification of mechanisms of self-healing

The mechanisms of self-healing have come into question especially when it comes to their contribution to water flow reduction in the initial stages of water supply. Most of the water permeation tests reveal a drastic water flow reduction within the first few days of water supply. Until recently, it has not been known which of the traditionally known mechanisms contributes to that drastic reduction. This prompted a one by one investigation of these mechanisms. Ikoma [4] performed verification tests of the contributory effect of each of the mechanisms (Figures 2-3 and 2-4), and found that they do not contribute notably to measured water flow reduction figures.

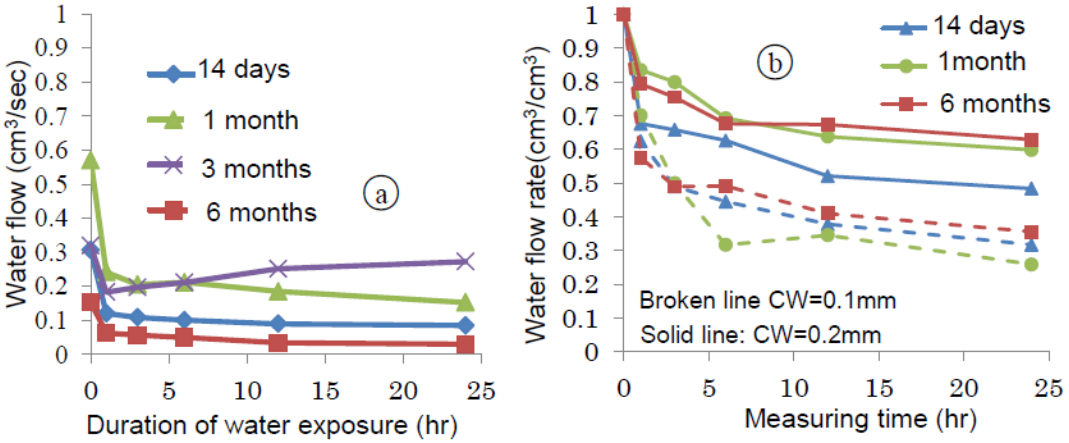

Figure 2-3: Verification of the mechanisms of self-healing concrete, hydration of unhydrated cement by comparing effect of age of concrete and crack widths (Ikoma, 2014)

This is what prompted the direct visual observation of water flow through concrete cracks, and finally pointed to the presence of large air bubbles that reduce the effective water flow. By investigating the effect of concrete age, and thus effect of unhydrated cement (Figure 2-3(a), plus the effect of crack sizes (Figure 2-3(b) it was found that the effect of various traditionally known self-healing mechanisms is quite insignificant in the initial stages of water supply.

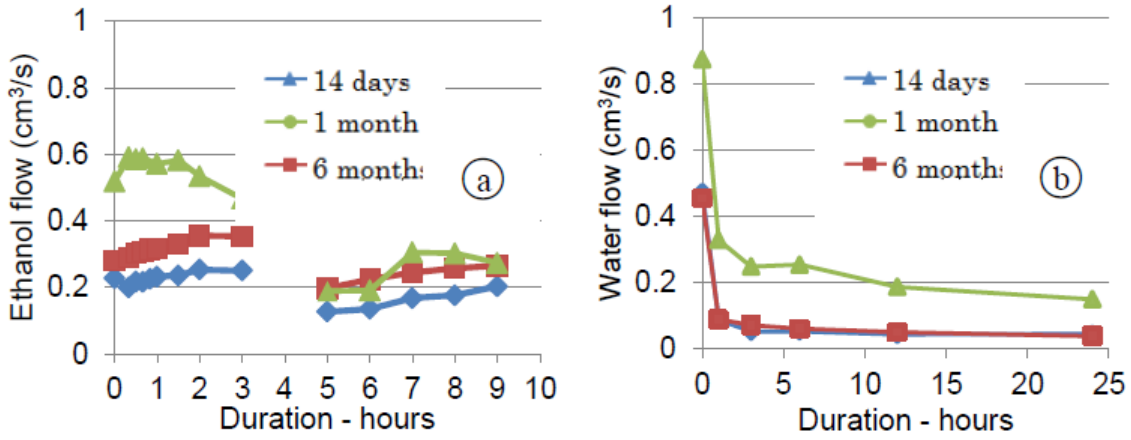

Figure 2-4: Verification of the mechanisms of self-healing concrete, effect of ethanol (a) and water (b) (Ikoma, 2014)

2.2 The nature of concrete crack surfaces

Cracks are an inherent part of concrete and determine its durability [8]. They are part of the nature of concrete, the result of chemical processes during hardening, or just during the service life of concrete structures. We cannot do away with them, but if they exceed certain limits, they may represent a bigger concern. When concrete cracks naturally, due to whatever cause, it results into two parallel crack surfaces. Self-healing concrete attempts to repair these, by 'gluing' them back together, or just filling up the gap between to avoid entry of any other elements. Concrete is a porous material, full of several interconnecting pores of varied sizes. Once cracked, this kind of pore structure is exposed on the surface of the crack. Any deleterious substance can thus penetrate deeper zones of concrete via these cracks and the extensive exposure of the fine pore structure.

2.2.1 Natural and machine cut surfaces

In reality, concrete cracks following lines of weakness, that's the natural trend [9]. Therefore any cracks in a real structure are rarely straight. They tend to be staggered

and with rough texture (see Figure 2-6). For self-healing testing, specimens are split allowing them to follow their natural crack path in case of similar environmental loading. This attempts to test the most expected situation in the real environment. Gang *et al.* [10] compared artificial and natural cracks of 0.3 and 1.0mm on their effect on water, and found that they behaved like an open surface that's exposed to the environment. The water penetration front agrees quite well with the geometry of the surface as shown in Figure 2-5.

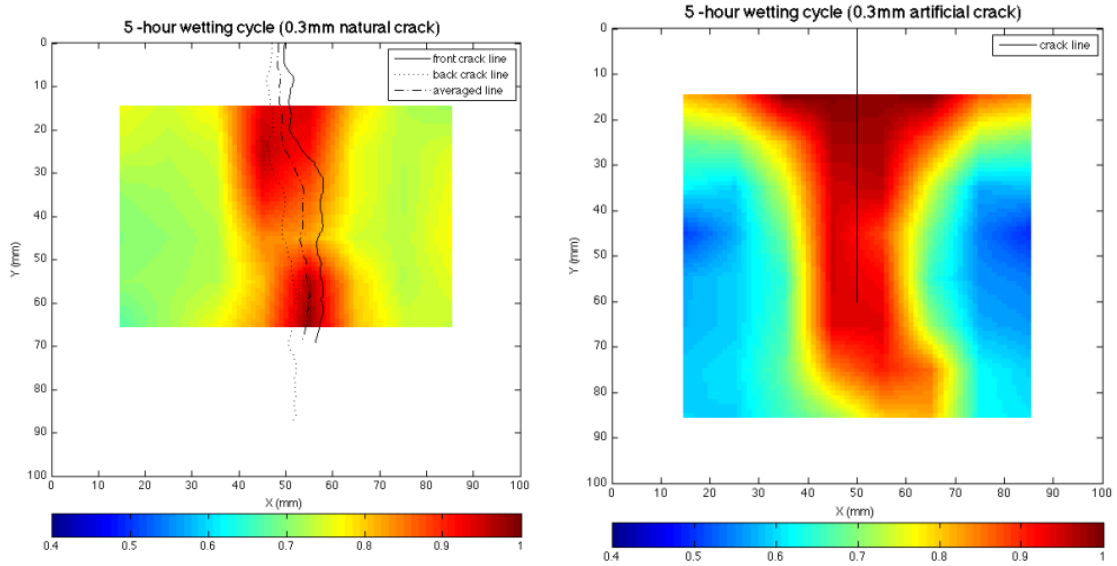

Figure 2-5: Simulation showing differences of wetting within 0.3mm natural (left) and artificial cracks (right) (Gang et al, 2015)

In order to simulate water flow through a concrete crack, and with direct visual observation via a parallel plane glass attached to a concrete surface, the concrete specimens are machine cut. This produces a straight line kind of crack, but still exposes the micro-pore structure of concrete. Naturally cracked surfaces too can be simulated, but not with glass. Using an acryl resin to mold the opposite crack side of one part of the specimen, a transparent material possessing a natural crack characteristic can be obtained. Machine cut surfaces lack the roughness of naturally cracked specimens.

Figure2-6 shows machine cut and naturally cracked specimens used for water flow testing. Water flow properties are different between the two types of cracks, with straight machine cut specimens having higher water flow rates than naturally cracked specimens considering the same gap width. This observation is expected, and is attributed to the complicated flow pattern in naturally cracked specimens and the straight water flow path for machine cut specimens. And yet to perform direct visual

observations, the machine cut specimen is best suited

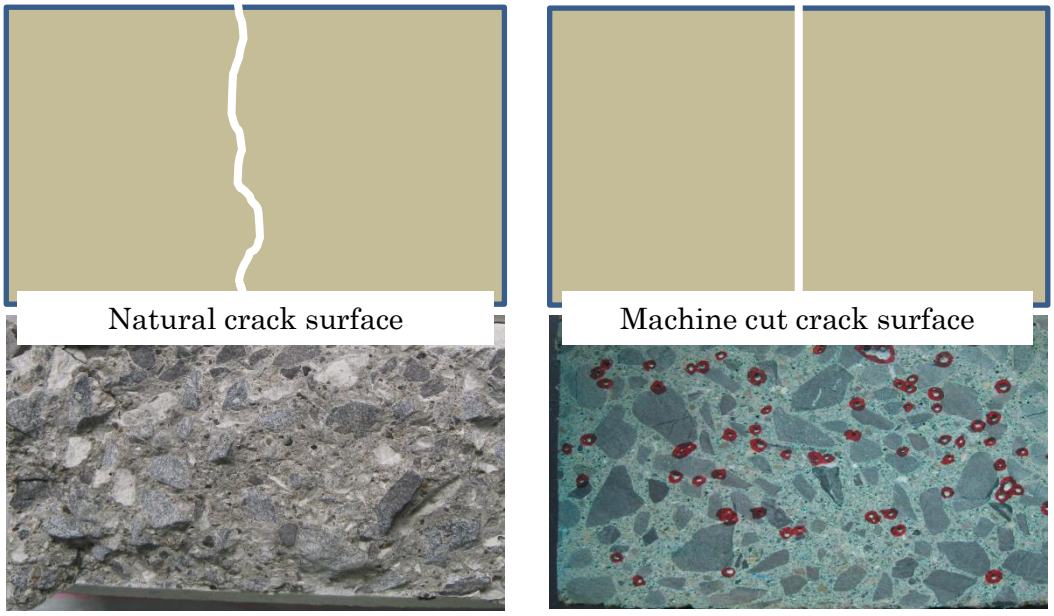

Figure 2-6: The nature of concrete surfaces; natural crack surface (left) are rugged and straight machine cut surface (right) is smoother.

2.3 Self-healing testing and water flow hydraulics

Water permeation into structural concrete is one of the biggest challenges for concrete durability. This is because water flow brings with it several chemical elements that attack the inside of concrete and compromise its service life, as well as durability. Chloride ion ingress comes via permeating salt water, and causes deterioration of steel reinforcements in structural concrete [11]. Carbonation too could be accelerated via similar water paths. So, the target of self-healing concrete is to quickly close up any water paths such as cracks that rapidly accelerate water permeation. Self-healing tests largely rely on the same principle – of supplying water into created cracks. By studying water flow reduction over time, we can ascertain the extent of healing that has occurred, probably through the mechanisms mentioned in section 2.1.1.

The Hagen Poiseuille equation of parallel plates is modified to compute water flow for concrete cracks (see equation 2). This modification caters for the material differences such as concrete surface roughness. Equation 2 is the modified Hagen Poiseuille equation for flow through concrete [12]

$$q_r = \frac{\xi.\Delta p.b.w^3}{12.\eta.d} \qquad \text{..... (2)}$$

q_r *is water flow of idealized smooth cracks,* Δp is differential water pressure between inlet and outlet of the crack, b is length of the crack (visible crack length at the surface of the structure), w is crack width, d is flow path length of the crack, and η is the absolute viscosity of water [2] .

By this equation, the basic hydraulics principles are expected to be obeyed. Thus, the crack width, and flow area dimensions, plus the water pressure head, are carefully monitored. For self-healing testing, if all conditions are kept constant, any water flow reduction is expected to be a result of self-healing, particularly tampering with the flow dimensions.

2.3.1 Water permeation tests for proving self-healing approaches

Water is used both as trigger for, and a measure of the extent of self-healing. The formation and deposition of calcium carbonate on crack surfaces is aided by the chemical make-up of water, and the nature of chemical composition of concrete.

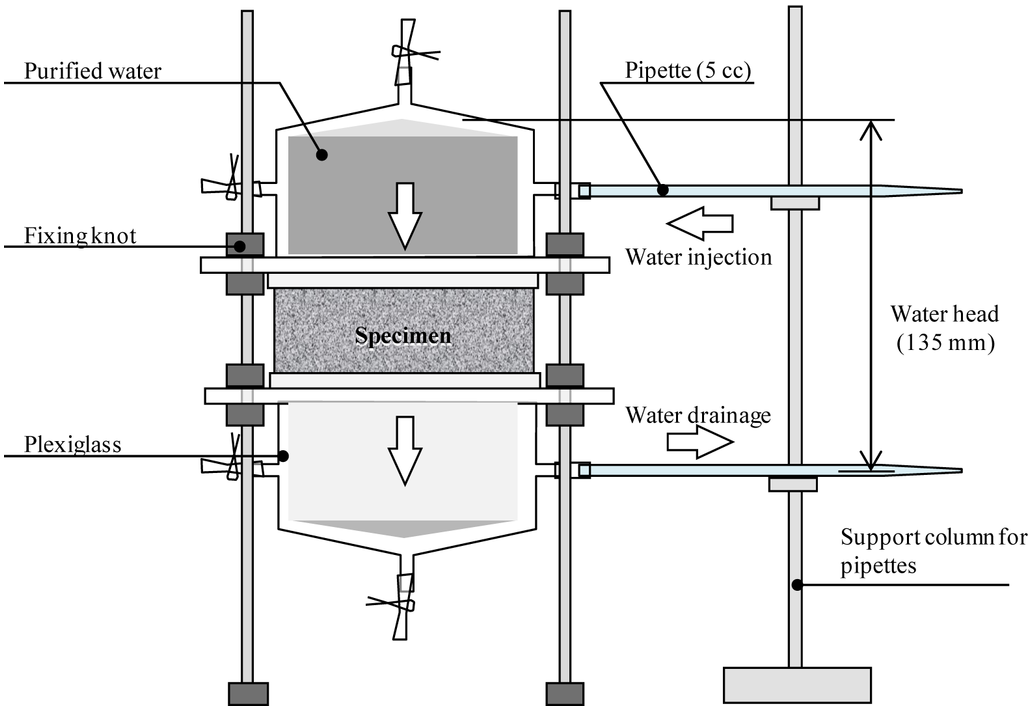

Figure 2-7: Apparatus for water permeability tests, adopted by Nishiwaki et al., (2014) for self-healing testing of concrete specimens [13]

By measuring the changes in outflow water (while ensuring a constant water head), we can be able to estimate the extent of self-healing. Thus, water permeation tests (Figure 2-7) for self-healing concrete rely on the results of water flow to prove their efficiency.

No wonder, most results of self-healing testing with water permeation describe a graph of reducing water flows against time, as shown in Figure 2-3.

2.3.2 Other self-healing tests

Besides water permeation tests, there are several other self-healing efficiency testing methods. These include visual observation of healing products inside cracked specimens, gas permeability tests (similar to water permeability), ultrasonic pulse velocity measurements, flexural and compressive strength measurements, Chloride permeability tests, and others [14]. Different healing efficiencies are obtained by different methods, and there is no singly and widely adopted test for self-healing testing! Probably the purpose of concrete should dictate what kind of tests should be done. If for example strength is important, then strength recovery via self-healing should be used as measure for efficiency of that particular type of concrete. And likewise is the instance where water permeability is an issue. In their review of the tests and methods of evaluating self-healing efficiency, Muhammad *et al.* concluded that the water curing condition was the most effective in terms of self-healing. They also gave shortcomings of available methods based on the literature studied, these are;

1. The lack to initiate the definition of self-healing efficiency. How do you classify the different levels of efficiency in self-healing?
2. Lack of availability of standard procedures or main referenced procedures to measure rate of self-healing.
3. Lack of adequate research on the length of the healed crack.
4. Lack of adequate research on the depth of cracked healed.
5. Lack to report the volume of crack healed.
6. Lack to report the speed of crack healing.
7. Lack to address the speed dynamic of crack healing versus concrete age.
8. Lack to address the structural crack healing.
9. Lack to address the durability of crack healing versus concrete age.
10. Lack of any quantitative data on the bonding strength between the concrete and the deposited material within the crack.

2.4 Water flow equations in hydraulics

In hydraulics, water flow is greatly documented, both for closed and open channels. Water flow in cracks is similar to closed rectangular flow for channels. For concrete cracks, flow has been approximated from the parallel plate theory flow. In this research, flow through concrete cracks is further expounded on, to probably reveal the effect of the exposed micro-pore structure on the surface of water flow.

2.4.1 Orifice and venturi flow considerations

Orifice flow refers to flow through a constriction in the direction of flow. It is important to some extent to hypothesize flow through cracks as orifice flow (see Figure 2-8). This could be considered true for the water pass tests where there is a water pressure head, pushing water through a narrow gap. On a small scale, the walls of these parallel surfaces (cracks) are not smooth, and are hugely characterized by pore depressions on both opposite surfaces. Figure 2-9 illustrates what it looks like in cracks with water flow and exposed pores.

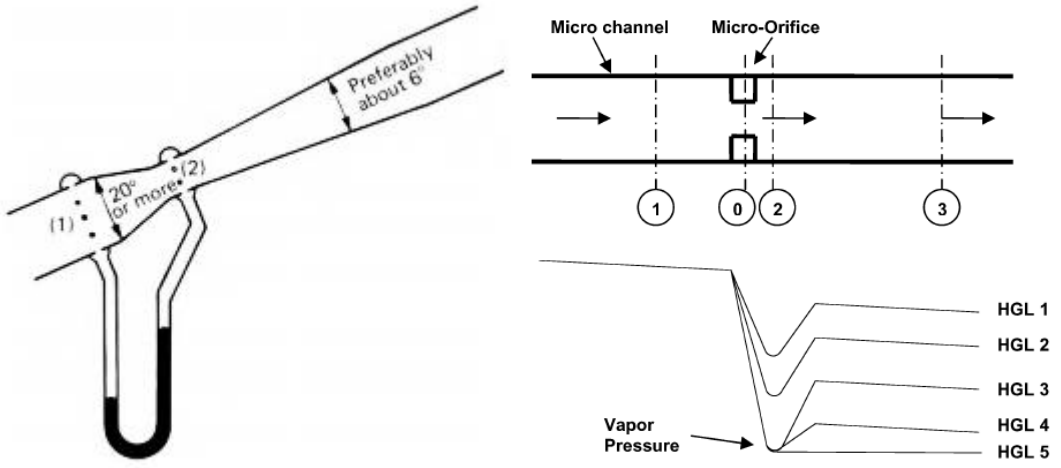

Figure 2-8: Figure showing effect of micro orifice in flow paths on the hydraulic grade line and flow pressure (Mishra and Peles, 2005) [15]

In order to conserve momentum, the Bernoulli equation suggests that velocity increases in and pressure decreases at the orifice [12]. Equation (3) shows the conservation of momentum for flow through orifices.

$$\frac{p_1}{\varrho g} + \frac{Q^2}{2gA_1^2} + z_1 = \frac{p_2}{\varrho g} + \frac{Q^2}{2gA_2^2} + z_2 \quad \text{..... (3)}$$

Where p, A, z are pressure, cross-sectional area and level readings at points 1 and 2. Q is the flow rate; rho is density and g, acceleration due to gravity.

In concrete cracks and at the pore, velocity is thus expected to decrease and pressure to increase. This kind of expectation contributes to the anomaly discussed in section 4.1 in Chapter four. Mishra *et al* (2005), studies and discusses the contribution of micro orifices to cavitation in micro channels. At the micro orifice, water flow pressure could equate to the vapour pressure and cause vapour bubbles. In connection with our research, these low pressures at such points would contribute to air evolution out of water especially for supersaturated water flow conditions.

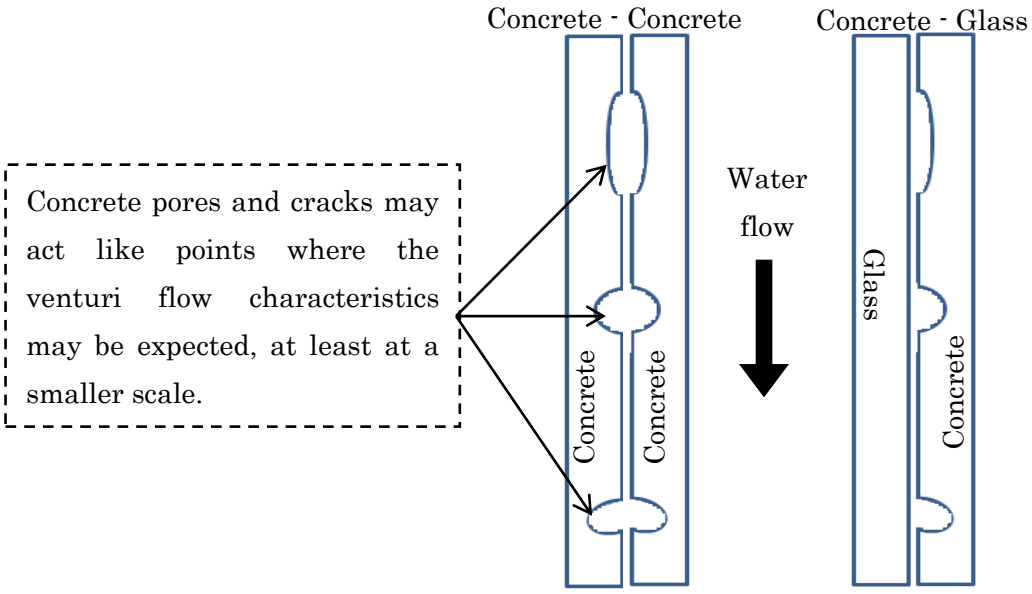

Figure 2-9: Concrete cracks are made up of pores and dents that on a smaller scale would affect the conditions of flow at those points

2.4.2 The parallel plate theory for laminar Poiseuille flow

On a small scale, concrete crack surfaces are assumed to remain parallel, and no wonder the parallel plate flow equation is modified to estimate flow through concrete cracks like in Equation 1. In simple terms, water too is assumed to be a Newtonian fluid, with zero yield force, and that there is no slip flow, i.e., no-slip boundary condition holds true. There is drag on the surfaces of the concrete, and due to viscosity, there is a velocity gradient [16]. The viscous forces are balanced by the flow pressure (via the constant water head in case of water pass test). The flow is assumed to be steady, and there is no 'time dependency'. For self-healing concrete, the flow path changes with time (due to mechanisms of self-healing) and so does the flow rate!

Figure 2-10 shows the consideration for flow between parallel plates, for an incompressible fluid with laminar flow.

Flow between fixed parallel plates Velocity profile

Figure 2-10: Velocity profile for flow of an incompressible liquid between two fixed parallel plates, assuming laminar flow conditions.

2.4.3 Laminar and turbulent flow in narrow gaps

Flow in narrow concrete cracks is assumed to be laminar. In the direct visual observation technique described in section 3.2, flow profiles characteristic of laminar flow are observed when coloured water and particulate matter are added to the water supply (see section 4.2). Streamlines are maintained throughout the specimen water flow paths. Figure 4-1 shows the nature of flow profiles observed during direct visual flow observation techniques.

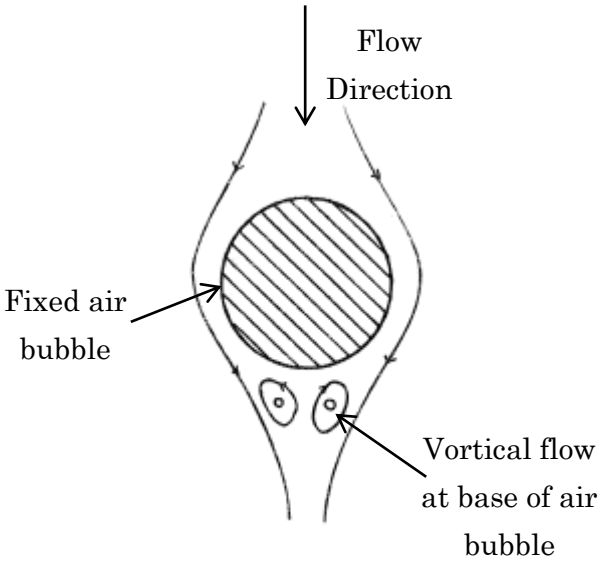

Figure 2-11: Illustration of the nature of turbulent vortices observed for flow at the base of the air bubble that's blocking water flow.

However, as the phenomenon of air bubbles actually changes the physical path of water, through growing air bubbles blocking water flow, certain amounts of turbulence can be observed at the base points of air bubbles in the direction of flow. Here vortices form,

and flow momentarily stops being laminar. A few dimensions down, laminar flow is created again. This kind of observation is a natural occurrence for any obstacle in the path of flow. Figure 2-11 shows an illustration of the nature of turbulent vortices observed for flow at the base of the air bubble that's blocking water flow.

Water flow in concrete cracks can be approximated as confined, and pressure driven. The hydraulic head is what causes flow to take place, and therefore water has to continuously be supplied to the water pass test set up. Concrete is a porous material, but given the dimensions of most specimens, water permeability perpendicular to the surface of flow can be assumed to be zero. Nonetheless, some of the tests were performed with a solid aluminium plate to investigate the flow dynamics around an air bubble with accounting for large surface flow effects. Figure 2-12 shows air cavities hinged at dents on an aluminium plate within 0.2mm gap spacing

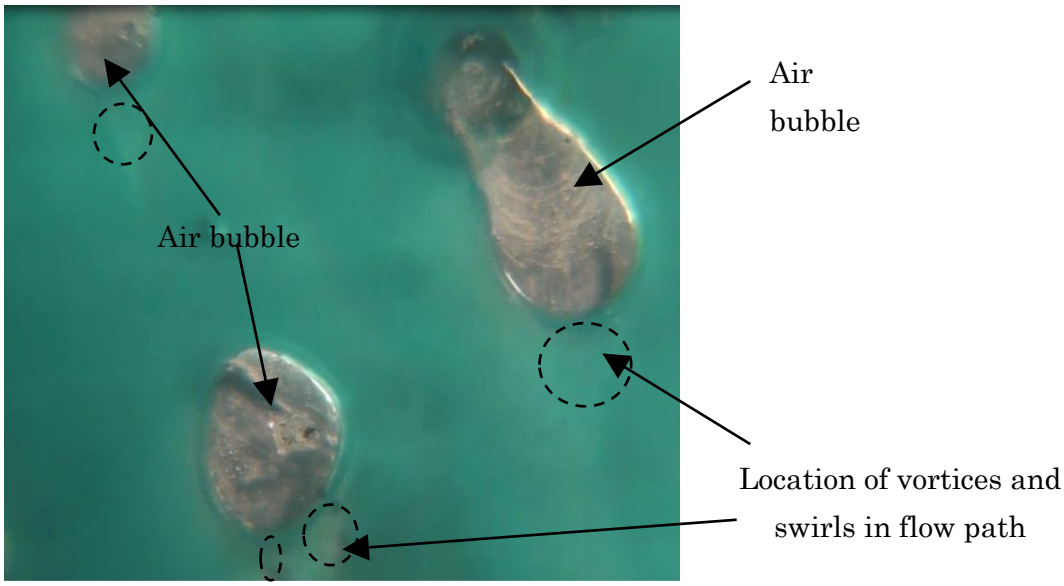

Figure 2-12: Air bubbles anchored within the path of water flow, with observed vortices at the base of the bubble. Coloured water is used to visualise the vortices.

At a micro level, all surfaces are not smooth, and especially for concrete surfaces. These may induce micro turbulence events at the boundary layer.

2.5 Chapter summary

In this chapter, the implication of crack self-healing testing by water permeation was investigated. This approach can be visualized as water flow through parallel plates and the modified equation of Hagen Poiseuille for parallel plates can be used to approximate

water flow characteristics through such cracks.

However, recent observations of air bubble in concrete cracks with water flow question the validity of the material factor used in the flow approximation equation, and to a large extent. Based on these observations, flow through concrete cracks is investigated and discussed. The possible hydraulics involved have been considered, such as water flow profiles, laminar and turbulent flow, plus the possible venturi flow within such surfaces.

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Chapter 3 Air bubble phenomena

3.1 Background to air bubble phenomena

The air bubble phenomena stems from our recent understanding of the mechanisms involved in self-healing. It comes at a time when great efforts are being invested in the development of various self-healing approaches in order to tackle the challenges of deteriorating concrete infrastructure. One of the common proofs for checking self-healing is the water flow recovery technique, which is performed using the famous water pass test as explained in section 2.3.1. This test produces results of flow rate against time, and most successful self-healing results show that water flow rate rapidly decreases in the initial stages of water supply, and stagnates or follows a lower rate of reduction. Figure 3-1 shows a typical graph of water pass test result [1].

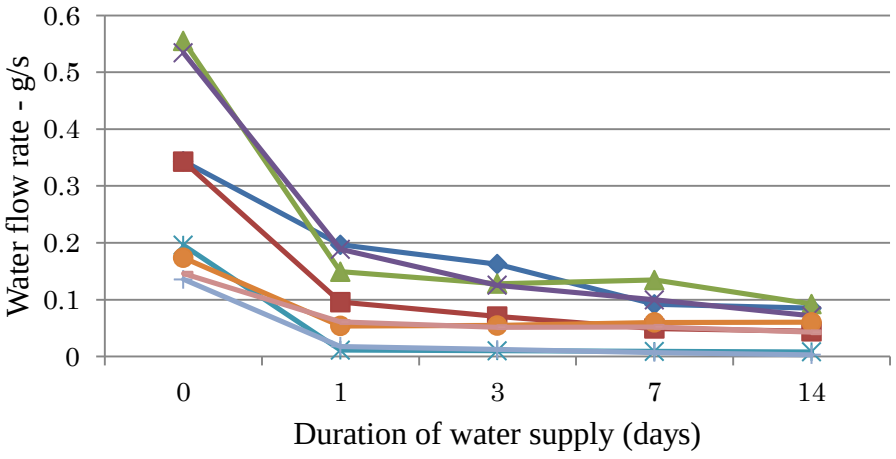


Figure 3-1: Water flow Vs duration results for several self-healing specimens for 14 days (Kayondo, 2014) [1]

This observation prompted the investigation into the mechanisms involved in contributing to such drastic water flow reduction. Ikoma [2] investigated one by one of the mechanisms in section 2.1.1 and found that they do not significantly contribute to the observed drastic water flow reduction. It was obvious that there must be another mechanism involved. This prompted the use of a direct visual observation approach, to directly observe water flow in concrete cracks, or to as much as possible simulate water flow through concrete cracks.

Water flow observation with this approach revealed large air cavities that were linked to water flow reduction that is observed in the initial stages of water supply, as shown in

Figure 3-2. It was concluded then that, large air bubbles block water-flow paths and this manifests in the form of reduced water flows. This created the background for further investigations of mechanisms involved in this new unconsidered and hidden mechanism of water flow reduction in concrete cracks. In most of this research the word 'cavities' and 'air bubbles' are used interchangeably to mean the same thing. As is largely the finding of this research, large air cavities start from small micro and nano air bubbles, and the difference could be in size only.

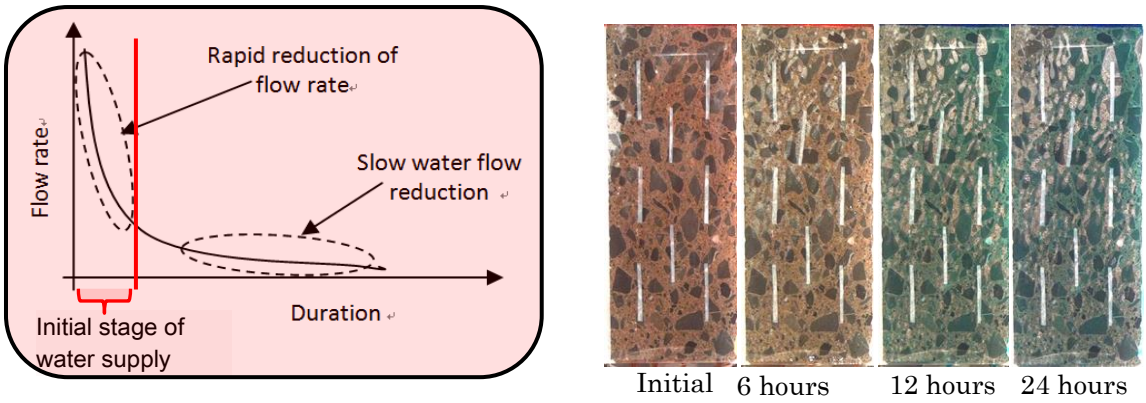


Figure 3-2: The initial rapid water flow reduction (left) is due to the formation of air cavities due to water flow in cracks (right), (Ikoma, 2014)

This chapter therefore attempts to understand the various mechanisms of air bubble evolution in water, and especially those that lead to air cavities in narrow gaps such as concrete cracks. The effect of these cavities is also quantified in a way, in addition to modifying the experimental set-up in order to minimize the effect of this phenomenon.

3.2 Direct visual observation technique for water flow in narrow gaps

Flow through concrete cracks is confined within the walls of concrete. Creating a direct visual observation approach, while still confining water flow, required the use of a transparent material and concrete. Acrylic resin was adopted and molded to depict the opposite crack-side topography. In addition, for machine cut concrete specimens, a plane transparent glass was used. The use of these enabled the mimicking of water flow through narrow gaps such as concrete cracks.

It is important to note that, in these direct visual observation approaches, only surface is that of a study material (such as concrete in this case); the other is either glass or acrylic and only provides a transparent media for visual observations. Water flow thus takes place on both surfaces, but the effect contributed by concrete is the focus of this research. Besides, the glass surface is assumed to be nonporous and with zero water

absorption during the water flow procedure.

Figure 3-3 shows the set up with both acryl and a plane glass for direct visual observation. With the use of a plane glass, the concrete surface is of a machine cut nature, while with acryl, the natural crack pattern is molded.

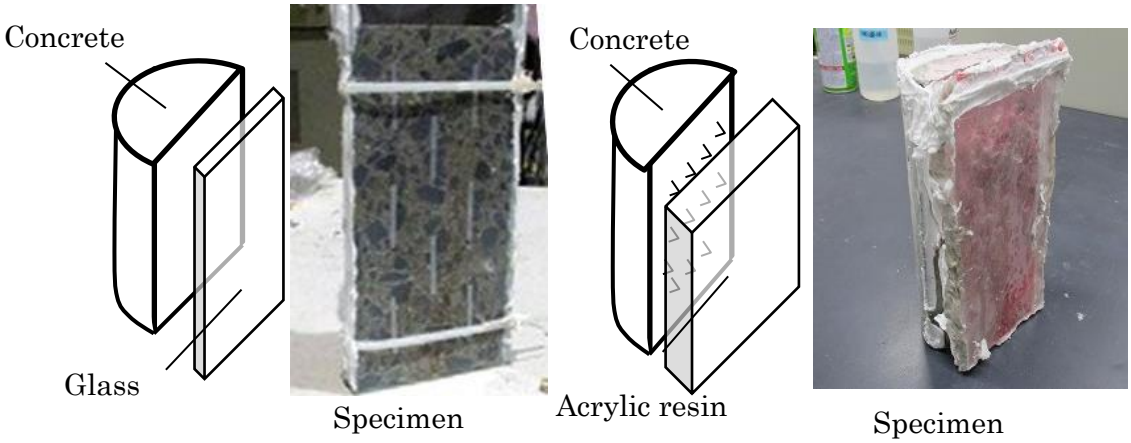


Figure 3-3: Specimen preparation for direct visual observation using either glass or acryl resin for one of the surfaces.

The set-up is built in consideration of the water pass tests. It thus still maintains a constant water head supply container which feeds the crack. Direct observation by the naked eye can be made, or even through video recording and photography. It is this kind of set-up that enabled the observation of large air cavities in the cracks of concrete having continuous water flow.

3.2.1 Experimental set-up and procedure

In order to perform a direct visual observation for simulated water flow through concrete cracks, one option is to use a plane transparent glass. The concrete sample is machine cut from a 200mmx100dia cylinder, along the height of the specimen. This produces a rectangular surface of 200x100mm. A glass plate measuring 200x100 is placed parallel and fitting to this surface and study gap (equivalent of crack width) is maintained by Teflon sheet strips. The sides are then sealed with either silicone or tape to create watertight sides and avoid any water leakage. The top opening of the gap is connected to a constant head water supply. In this case it's an 8.5mm UPVC pipe measuring the same diameter as the concrete specimen (10mm). The entire specimen is sealed with silicone to only leave two openings, water supply and water outflow points. Figure 3-4 shows the experimental set-up adopted for these observations and water flow

measurements. The water flow test proposed by Morita for self-healing testing is further modified to enable a combination of both water flow measurements and direct visual observations [3].

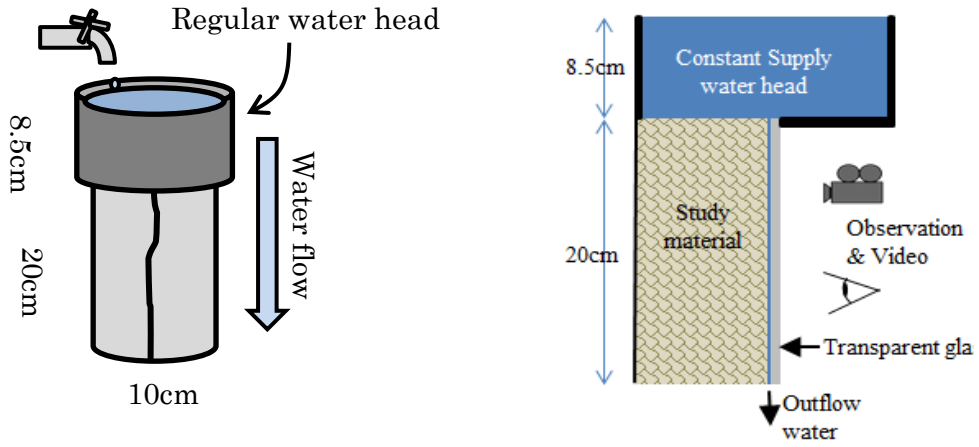


Figure 3-4: Water flow testing procedure for closed concrete cracks (left), Vs the visual observation approach for water flow (right)

The observation set-up is facilitated with external lighting, for video recording or naked eye observation. Once water flow is supplied to the specimen, care should be taken to confirm that there are no leakages. If any, they should be sealed before flowrate measurements are started. The test involves the use of coloured water (blue/green/red) to provide the necessary contrast for air bubble observations, especially for video recording observations.

The testing procedure has been continuously adjusted to ease measurements and to validate the nature of experiments. The initial specimen conditions for example have been changed from natural conditions to vacuum water soaked specimens in a fully water saturated state. These conditions are later investigated case by case.

3.3 Air bubbles in concrete cracks with water flow

In 2014 when Ikoma observed the blocking effect of water flow by air bubbles, it wasn't so clear the origin of air bubbles. At we first, it was thought to be air contained in concrete coming out with real-time water permeation and being trapped within the gap of glass and concrete surfaces. When vacuum soaking was performed, and water pass tests redone, still air bubble growth was quite significant. The effect of concrete-trapped air was now removed from the equation. Focus now turned to the characteristics of water supply, and it then became clear that flowing water contains air and there must

be a way by which it comes out. This kind of hypothesis formed a strong background for later experimentation in an effort to understand the mechanisms of air bubble creation and growth within the narrow gaps of concrete cracks. Figure 3-5 shows air bubble growth sequence against time, for a 24hr period with mortar specimens initially saturated with de-aired water and then supplied with tap water in the 24hr period.

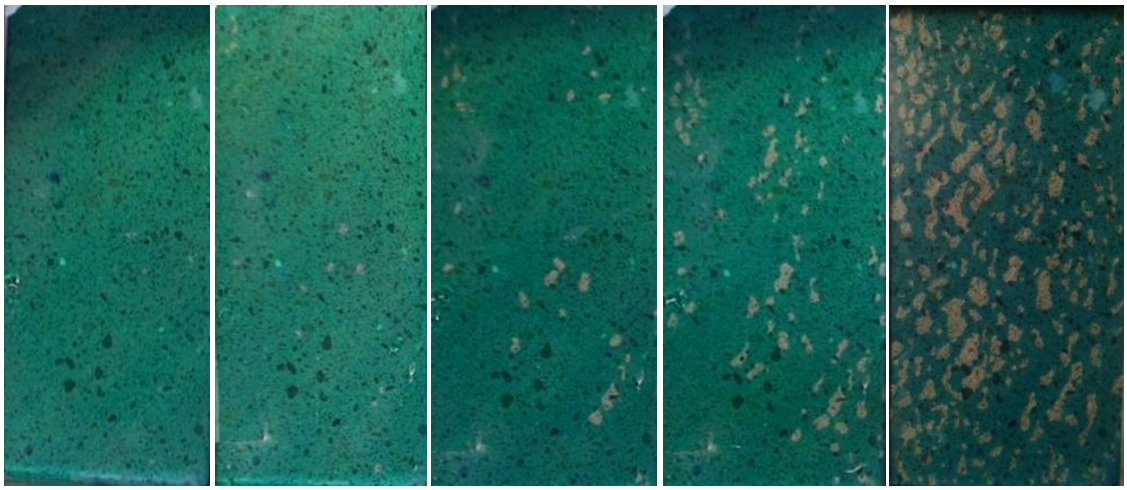


Figure 3-5: Air bubble developed on an interface of mortar and glass with 0.2mm gap spacing, under continuous tap water flow for 24hrs.

With continued water flow tests and direct visual observation approach, a pattern could be noticed for the formation of air bubbles. Even for the same specimen with the experiment repeated several times, it was clear that air bubbles preferred to be formed/ created at certain points on the surface of the concrete specimens.

Figure 3-6 shows a pre-marking of the expected air bubble locations on the external surface of glass (above), and performing water flow tests to ascertain the hypothesis (below in figure). Air cavities preferred to be located at concrete pore or depressions within the surface of water flow (see also Figure 3-9).

Further investigations revealed that different cementitious surfaces, of mortar, paste, or concrete produced different configurations of air bubbles. The effect of different material surface is further expounded on in section 5.9, Chapter 5. The natural state of cracks caused the highest air bubble evolution because of the presence of initially trapped air bubble nuclei that quickly grow to constrict the paths of water flow. The air cavities would then be separated by thin streams of permeating water flow and high capillarity forces. Flow almost becomes zero, and only exists to maintain the presence of

strongly fixed air bubbles. It is expected that the effect is doubled when both interfaces are of concrete, such as in closed concrete cracks.

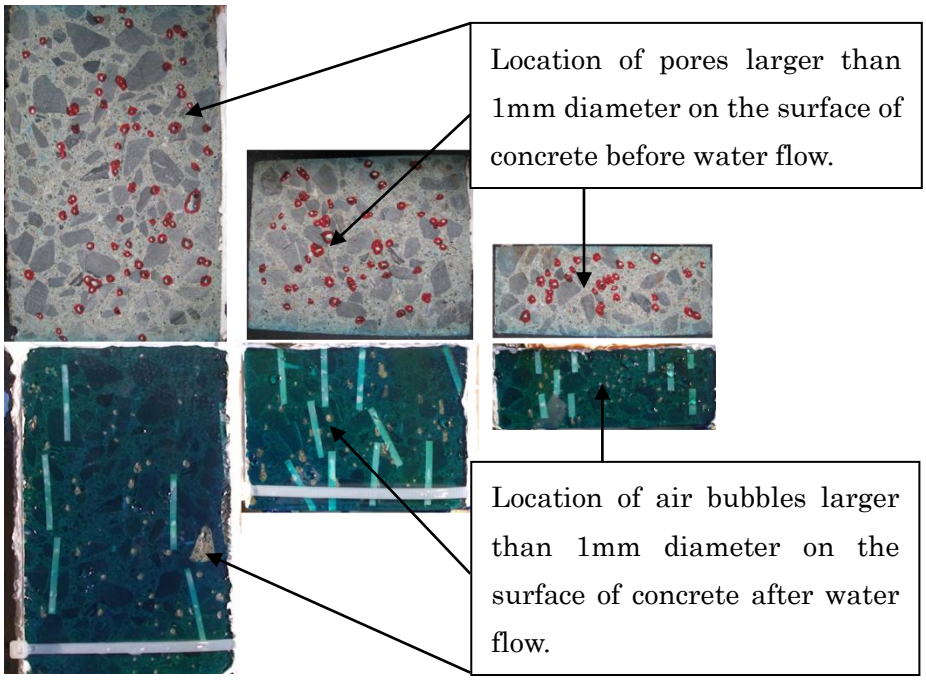


Figure 3-6: Tracking the location of air bubbles before water flow tests (above) and then comparing with the result (below)

3.4 Air bubbles in porous media with water permeation

The air bubble phenomenon is not unique to water flow in concrete cracks alone; and apparently it's not a new thing! In geotechnical investigations involving water permeation through porous media, air bubbles have been observed to be formed during the process of water percolation. Unfortunately, not much has been documented on their mechanisms of growth or details of why. They have been regarded as a nuisance in testing especially when super-air-saturated waters are used. Figure 3.7 shows air bubbles creation as a result of supersaturated water permeation through sandy media [4].

In water treatment plants, which too rely on the use of porous filtration membranes, the effect of air bubble growth was observed – and in a way of affecting filtration flow rates. Here, degassing was used to try and overcome the challenges of 'clogging' caused by air bubbles in the system. Figure 1-2 (Chapter 1) shows the result of using supersaturated waters in water treatment facilities using sandy media. Air bubbles are observed in the system and create a menace for the filtration systems [5].

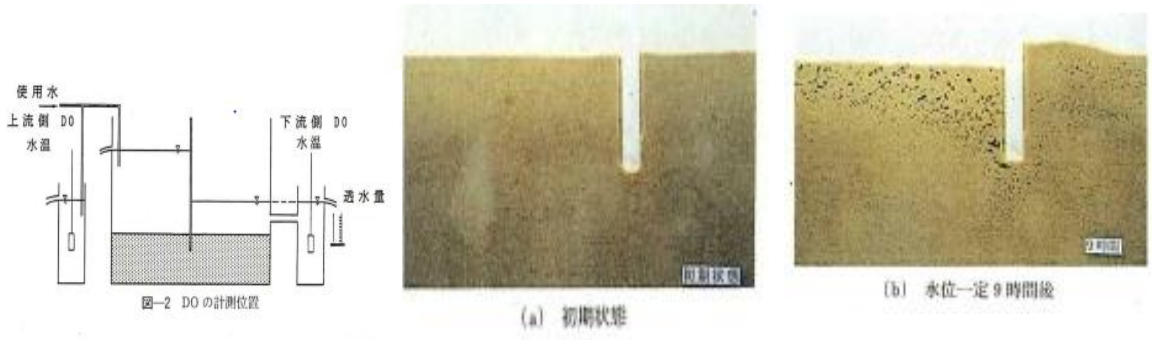


Figure 3-7: Air bubble creation in sandy soil media due to seepage of supersaturated water. (Kodaka and Asaoka, 1994)

In all these cases, air bubbles have been documented, and their direct effects on the involved processes enumerated. What has been lacking is an attempt to try and understand the underlying mechanisms of this phenomenon of air evolution from water in porous media.

In contrast to direct water permeation through a porous sandy media, air bubble growth in concrete cracks is not direct permeation through the material pore structure; it is due to water flow between two porous concrete surfaces. The air bubbles that are created are hinged on the concrete surface and extend into the flowing water (see Figure 3-8). As has been observed with concrete surfaces, it is expected that since porous sandy media have similar properties, air bubbles grow in the same way.

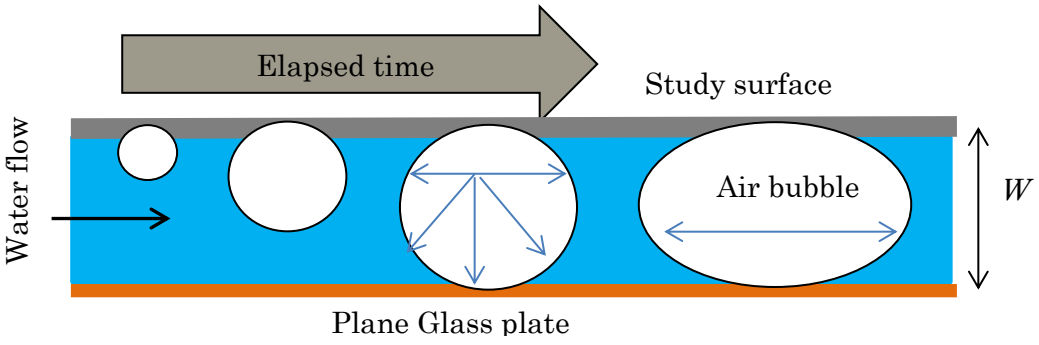


Figure 3-8: Illustration of air bubble growth that is observed within narrow gaps with water flow. Air bubbles are hinged on to the study surface and increase in volume as time passes.

In some of these isolated cases [4], [5], [6], these air bubbles are observed to be stable and their effects long lasting. Peck (1969) relates the anomalous slow release of water in some outflow experiments to the slow growth of entrapped bubbles, and their stability

on the large capillary potential [6].

3.5 Categories of air bubble evolution from water

3.5.1 Air bubbles in bulk water

Air naturally exists in water. It is at least necessary for the survival of living organisms in water (plants and animals) [7]. At any given temperature and pressure, there is an equilibrium level of air concentration in water. Air is soluble in water, and its solubility is governed by Henry's Law, which states that the mass of a dissolved gas in a given volume of solvent at equilibrium is proportional to the partial pressure of the gas. Air in water exists in the form of dissolved single molecules, to large air cavities and bubbles [8].

Air bubbles in bulk water exist in various sizes; from nano, micro and even large millimeter size air bubbles. Large air bubbles quickly rise out of the bulk water by buoyancy, and are also easily formed again by water movements and waves (especially for open water bodies). In pressurized water, such as tap water, dissolved air content is usually very high. This type of water if opened to the atmosphere is actually supersaturated, and air bubbles will form quickly and rise out of the container in which the water will be contained. The definition of the term nucleation would be appropriate at this stage. With reference to air bubbles, nucleation refers to the initial stage/step in the formation of an air bubble. For air bubbles in bulk water, nucleation occurs at points of lowest energy requirements in the system. Air bubbles will start to nucleate on the sides of the container in which tap water is contained [9]. Figure 3-9 is an illustration of heterogeneous nucleation at an existing pocket within the surface. Micro and nano bubbles contained in tap water tend to be more stable than the larger air bubbles, and stay suspended in the water floating about [10], [11].

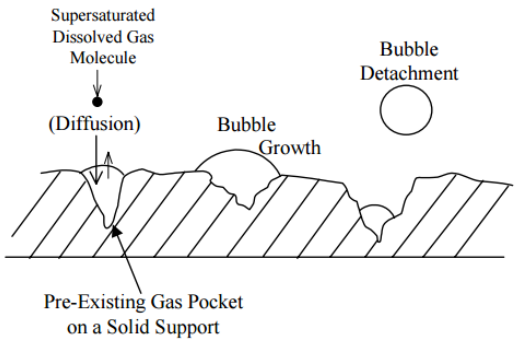


Figure 3-9: Heterogeneous nucleation of an air bubble at an existing gas pocket within the water bulk or container (Scardina, 2004)

In relation to the findings of this research, the observed fixed air bubbles within the narrow gaps of water flow are linked to this kind of nucleation mechanism, which is then supported by the conditions that exist within narrow interfaces of water flow.

3.5.2 Cavitation and its concept

Cavitation is the process of nucleation that occurs when the pressure falls below the vapour pressure of the surrounding liquid. If this happens, the air contained in the water has to obey Henry's law dynamics, and thus leaves the water to form bubbles. It is like boiling water, but without supplying heat! If there is no air in the water, then water vapour forms cavities [12]. The phase change from liquid to gas in a very short time, caused by a pressure reduction below vapour pressure is what is classified as cavitation. This is the concept of cavitation. It leads to the formation of micro and nano bubbles, which die away very quickly releasing energy in form of heat or sound. It involves considerable energy exchange and transfer [13].

Compared to the air bubbles observed in this research, cavitation is totally different. The air bubbles observed here are those that grow in size because they are trapped /fixed at nucleation sites within narrow interfaces. Their growth isn't instant, and they are stable within the narrow gaps.

Additionally, cavitation phenomenon is usually violent and capable of causing damage due to the high amounts of energy involved. It has thus found applications in cleaning systems, or where it occurs, attempts at reducing its impact are put in place [14]. In cavitating flows, the complex micro-fluid-mechanics associated with the bubble interaction with solid boundary has been investigated by Brennen [15]. The noise from these individual cavitating bubbles plus the associated scaling phenomena reveal the comparable difference between cavitation and the air bubble mechanism in our research.

3.5.3 Degassing

Degassing is also a means to expel air from a solution. Since dissolved air obeys Henry's law, degassing can be achieved by lowering ambient pressure. This would cause air to leave the liquid. By using a vacuuming pump to cause negative pressure, water can be de-aerated.

With the understanding of air bubble formation in concrete cracks, self-healing testing procedure involving water permeation was adjusted. Specimens were vacuum soaked and de-aired water used for permeation tests. All this was possible by the possibility of

degassing, to cause air to leave water by applying a negative pressure. This category of air evolution from water is also not similar to what was observed for narrow gaps. The anomaly of this observation compared to what is expected is explained in section 4.1.

3.5.4 Boiling

Boiling is another approach by which air can be caused to come out of water. It involves raising the temperature of water to its boing point. Vaporization takes place and gas is formed. Nucleate boiling leads to formation of small air or vapour bubbles at discrete points on the boiling surface. Still, boiling changes the equilibrium condition for gaseous absorption into water. Air instead is forced to come out of water and obeys Henry's law. In this research, the mechanism of air evolution from water is different from boiling as there is no temperature change that takes place (it is currently assumed so).

3.5.5 Scope of air bubbles in this study

In this study, air bubbles are considered to be air cavities that are trapped or fixed within narrow gaps with non-zero velocity. The air bubbles co-exist against the direction of water flow.

Bubble sizes may vary from nano, micro, submillimeter and to several millimeters large trapped air bubbles, depending on the ambient conditions. The smaller air bubbles are capable to increasing in size or even reverse growth, as long as certain conditions are met. Section 5.3 elaborates the conditions necessary for these kinds of air bubble growth. Figure 3-10 shows the scope of air bubble categories investigated in this research

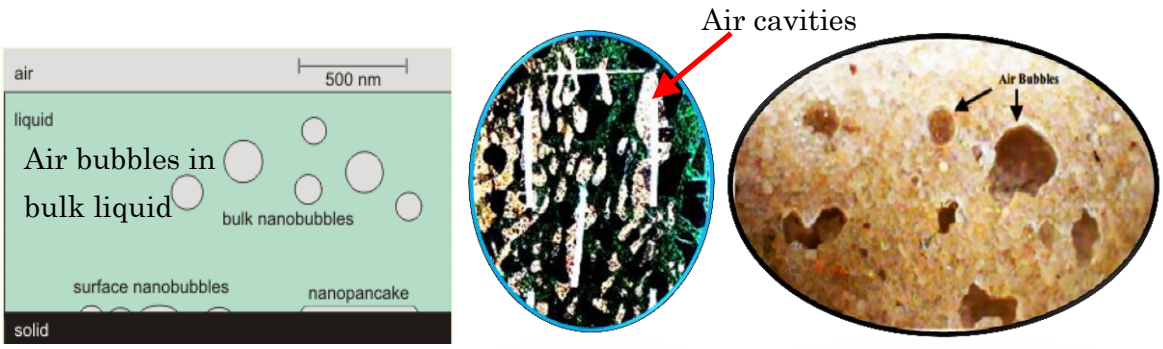


Figure 3-10: Scope of air bubbles studied in this research: air bubbles fixed on the surface of water flow in narrow gaps.

3.6 Quantifying the effect of air bubble growth on water flow

Air bubble growth has strongly been proposed as the cause of the drastic water flow

reduction observed for most self-healing water permeation tests. It is therefore necessary to understand the kind of correlation that exists between air bubble growth and water flow reduction.

3.6.1 Image analysis using ImageJ software

In order to clearly compute air bubble growth, and to quantify the total correlation between water flow and air bubble growth, ImageJ software analysis was performed for the instantaneous images taken at every time of water flow measurement [16]. The software is able to differentiate between pockets of air and water flow paths. The pockets of air (air bubbles) are then computed in terms of area and pixel density. A standard specimen surface area (17x10cm) is used to represent the total surface over which water can flow. The difference in initial specimen conditions can be captured by ImageJ analysis of the zero hour image of the specimen.

Figure 3-11 shows the analyzed images, with air bubbles clearly distinct from water flow spaces. With this kind of image analysis, air bubble growth can be tracked from the small submillimeter bubbles to the large centimeter long air bubbles. The total area occupied by air bubbles at selected times of water flow measurements can be correlated to the water flow and the total effect enumerated for a given measurement duration. With this, we can compute and compare the effect of different amounts of interface on water flow.

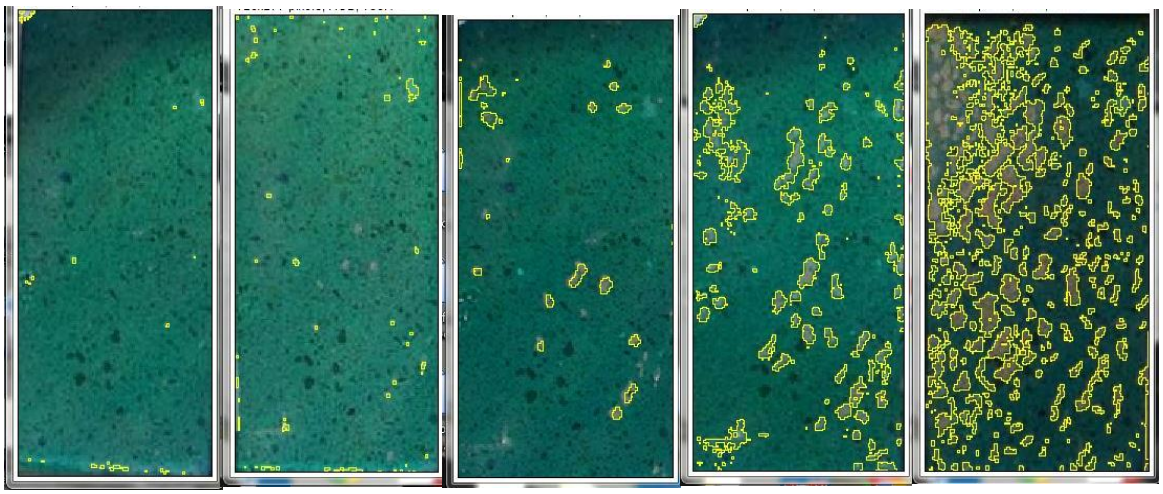


Figure 3-11: Image analysis of air bubble development and growth for a mortar specimen. Yellow boundaries represent air – water interfaces (air bubbles)

3.6.2 Bubble growth Vs water flow reduction

The visual observation and video recording approach has simultaneously been done with water flow measurements over a given period of time. In these experiments we are able to track air bubble growth with water flow amounts at any given time. By getting instantaneous water flow amounts and the size of the air bubbles, we can track how the two variables change.

It is important at this stage to distinguish between the two causes of water flow reduction in these measurements:

1. Water flow blocking: This is what happens when large and sizeable air bubbles block the flow of water within the narrow gaps. The air bubbles in this case interface with the two boundaries of water flow within the cracks/narrow gaps, and water flow reduction is largely due to their path narrowing mechanism. This is the understanding that explained Ikoma (2014) findings of air cavities leading to water flow reduction instead of the traditional mechanisms of self-healing. Since it takes quite some time to achieve total growth (plus other necessary conditions), the effect of this mechanism could be observed after several hours (About 5 hours minimum)

2. Water flow braking: This happens when the air bubbles are still in 'infancy' – before they develop into large air bubbles stretching across the water flow gap (see section 6.2.1). When air bubbles are still small and anchored at their nucleation points, a larger part of their surface is exposed to the flowing water. By the anchorage provided by the solid surface/ nucleation surface, air bubbles stay hinged and resist any wash out; in doing so, they act as *water flow-brakers*, and this is how the water flow braking takes place, by utilizing the characteristics of the air – water interface. The mechanisms involved are explained in chapter 6 and 7.

It is implied that the mechanism of water flow reduction within the first 2 – 3 hours of water flow occur due to the effect of air – water interface at the not fully grown air bubbles for the initial condition (vacuum water saturated specimen) in Figure 3-13. Beyond the third hour, water flow reduction is a combination of both water flow braking and blocking mechanisms, and it's difficult to distinguish between the two, experimentally. In Figure 3-12 air bubble growth is tracked for a concrete specimen in its natural state (partially saturated initial condition), and for this, water flow braking is observed to occur towards the end of the end of the 1st hour of water flow.

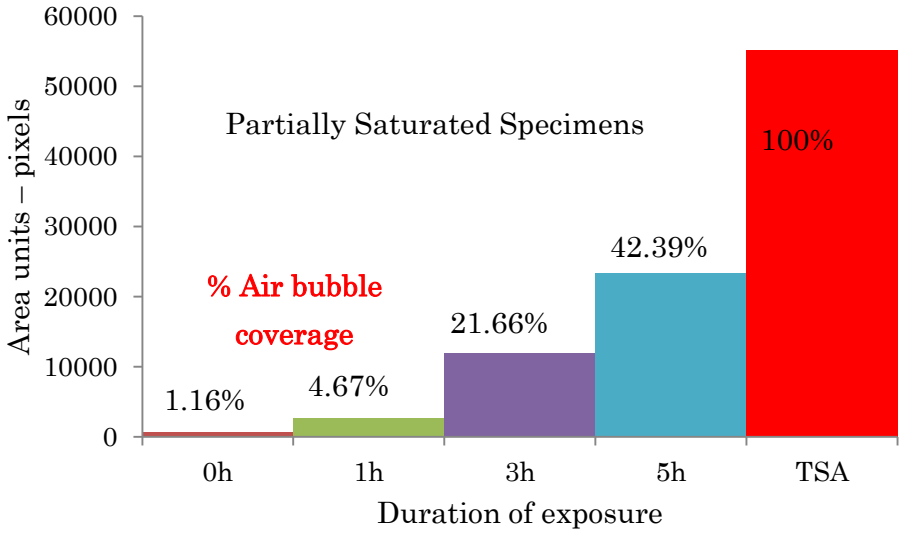


Figure 3-12: Air bubble growth area as analyzed by ImageJ software and compared to the total surface area (TSA) for a partially saturated specimen

It could be possible to measure the water flow reduction due to braking effect only, though it would be difficult to physically trace and enumerate the number and size of air bubbles causing this amount of water flow reduction.

When Figure 3-14 of water flow amounts is superimposed on Figure 3-13 for the same specimen, additional comparison can be made. The negative correlation that exists supports the initial hypothesis of decreasing water flows due to the braking and blocking effect of air bubbles. Relatively large air bubbles can be traced from 100micron size to large millimeter sizes. Through continuous video recording, air bubble growth has been observed. Stability of air bubbles too, has been observed. Despite continuous water flow, air bubbles are observed to stay 'hinged' at their nucleation points.

Air bubble growth observations have largely been performed on cementitious specimens since they created the background for this kind of investigation. However, in order to dissociate the observed phenomena from the possible effect of air contained in concrete, additional observations were performed with a dented aluminium plate. The dents were to mimic the porous nature of concrete surface. Figure 3-15 shows air bubbles hinged or anchored at the dents within a 0.2mm narrow gap bound between the dented aluminium plate and glass.

Similarly, and for other materials, the air bubble phenomena could be observed and its associated water flow reduction enumerated. Their exist differences in the rate of growth and observed sizes of air bubbles for the different materials, and details of these

are discussed in Chapter 5.

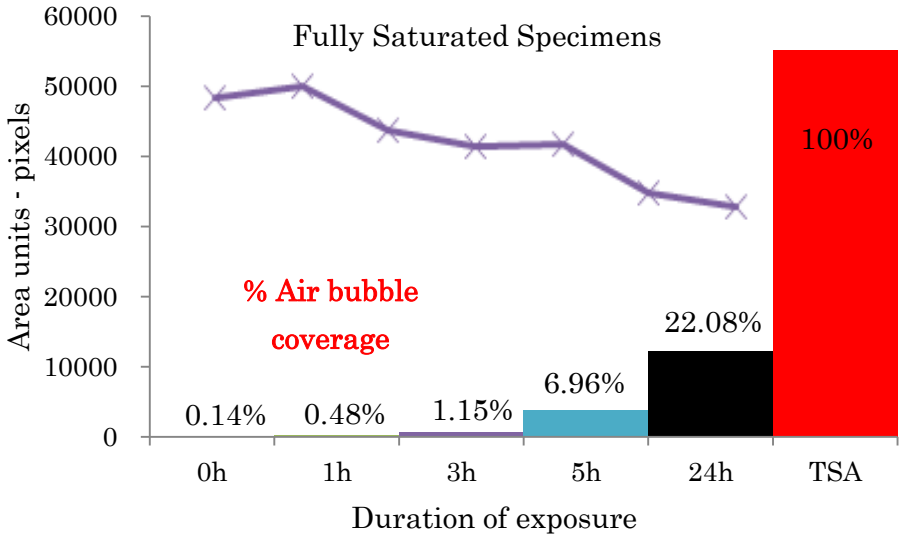


Figure 3-13: Air bubble growth area as analyzed by ImageJ software and compared to the total surface area (TSA) for a fully saturated specimen

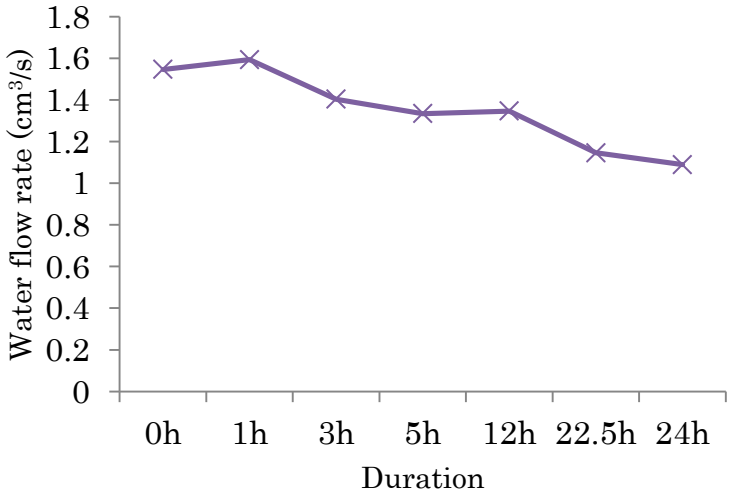


Figure 3-14: Water flow Vs duration graph for a fully an initially water saturated concrete specimen

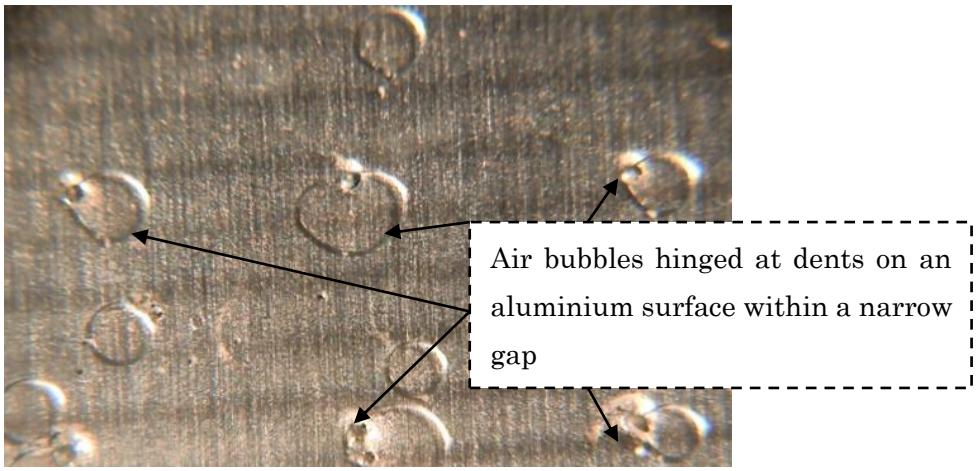


Figure 3-15: Air bubbles hinged at dents on an aluminium surface enclosed with a glass plate to create a narrow gap of 0.2mm

3.7 Modified method for water flow tests

It is has become clear that air bubbles change the characteristics of the flow paths, especially in narrow interfaces or micro pore structure. Figure 3-16 illustrates the hypothesized effect of fixed air bubbles on water flow braking and the extent of this effect on water flow in narrow gaps.

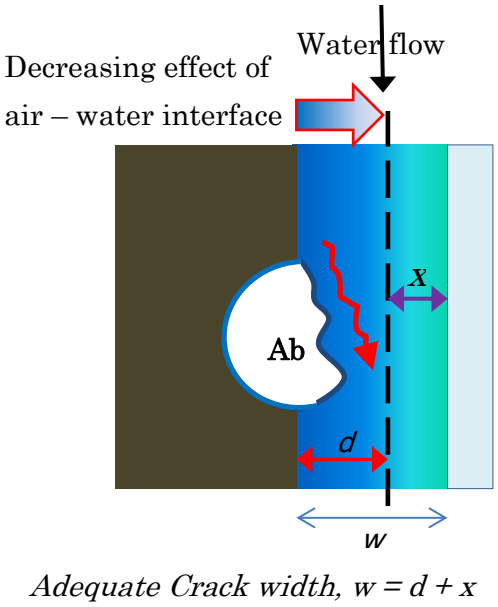
Concrete self-healing tests mostly rely on water flow through cracks to ascertain extent of recovery. This would indirectly reveal the potential for any proposed self-healing approach. It is thus important that, the method used to test any self-healing approach be foolproof! With our recent findings of air bubbles contributing largely to water flow reduction in narrow gaps such as concrete cracks, it is important to either modify the approach or change the testing method altogether. Given what we know, of the conditions necessary for air bubble growth, the water flow test should be modified appropriately to avoid the over estimation of self-healing efficiency.

1. The use of supersaturated water should be avoided completely while performing water flow permeation tests.

2. De-aired water is recommended for water flow tests. It is almost impossible to get rid of all air from water, but de-aired water will help minimize any air bubble associated challenges.

3. Based on the results of several water flow tests, it is recommended that a minimum starting crack width of 0.3mm be adopted for any concrete self-healing tests using water permeation. Air bubble growth is not favoured for large crack widths. This is

due to the increased speed of water flow in such gaps.



d represents the region within the narrow gap where the air – water interface anchorage phenomenon causes water braking and thus flow reduction;
Beyond ***d***, a distance ***x*** represents the region where air bubble effects seize to exist. This is the region where other self-healing mechanisms/approaches may contribute to water tightness recovery in concrete cracks. ***w*** represents the total crack width *(d+x)>= 0.3mm*

Figure 3-16: Illustration of the hypothesized effect of fixed air bubbles on water flow braking and the extent of this effect

Beyond these modifications or suggestions, it is important to check internal crack surface for any healing products. Figure 3-17 shows considerations for minimum crack widths and

The famous water pass test for self – healing testing requires some slight modification in the procedure (Morita, 2010), see Figure 3-4. The current procedure doesn't dictate on the quality of water supply. Direct supply of tap water has been associated with creation and growth of air bubbles within the crack gaps.

The new proposed method would require the adoption of a minimum crack width, and the use of de-aired water. The setting of initial conditions of specimens should be adjusted. The specimens should initially be vacuum-saturated with de-aired water, and entry of air pockets avoided. Water should at all times be maintained in the supply water head container. During the continuous water supply process and all testing procedures, the use of de-aired water should be maintained.

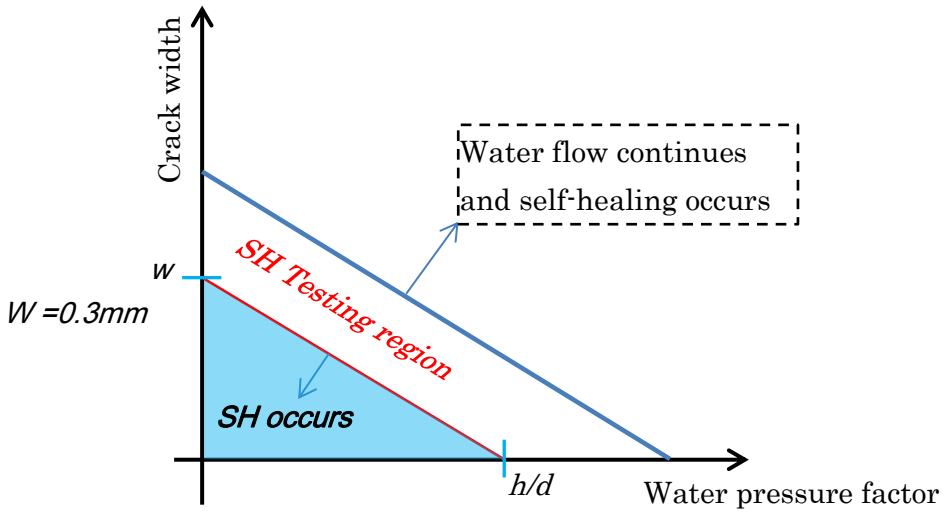


Figure 3-17: Illustration of adequate conditions for water permeating self-healing testing

3.8 Adequate crack width for self-healing testing

Self – healing testing aims to check actual recovery of a material when damage occurs. In concrete technology, crack self – healing testing seeks to recover a cracked portion of a concrete to specific recovery standards. Water tightness recovery is one major task of self – healing technologies. Testing of self – healing approaches for this particular task requires actual or reliable recovery of a given section of cracked concrete. Water flow through such cracks generates static air bubbles in the self – healing system. These mimic water flow reduction that is usually caused by actual healing products deposition in the crack gap. The creation and stability of these air bubbles in crack gaps would make it difficult for meaningful self – healing to take place.

In order to achieve meaningful results for self – healing testing, there must be either a means of completely ridding the system of air bubbles or of not giving them a chance to prevail. The latter can be achieved by setting a stringent testing method. It is almost impossible to rid air of dissolved gasses, as long as it is exposed to atmospheric conditions. Setting a stringent testing method involves proposing a minimum crack width for self – healing testing. Given what we already know of the effects of air bubble creation on a water flow surface in narrow gaps of water flow, it is only necessary that minimizing this effect as much as possible is one easy way to test the efficiency any self – healing technique. Therefore, a faster flow rate, achieved through either a higher

pressure head, or wider testing gap are away to minimize the effect of air bubbles created in the water flow system. Additionally, avoiding the use of supersaturated water during testing should be adhered to. Pressure flow tests for self – healing test should achieve a trade-off relationship between water head and crack width. And there exists a range of values where the right combination of these variables (crack width and pressure head) permits self-healing to be achieved. Beyond these, self – healing is impossible, and below, self – healing will definitely take place and the effects of air bubbles can't be ruled out. Figure 3.17 shows a depiction of the trade-off relationship between pressure head and crack widths.

Water permeation tests are not the only tests for self – healing, there are other methods that can be utilized to prove the efficiency of self – healing techniques.

3.9 Utilisation of air bubble generation concept for self-healing.

The creation of air bubbles in crack gaps by supplying supersaturated water appears as a nuisance for attempts to come up with meaningful self – healing. By modifying the interface where healing products are meant to be deposited, nano and micro air bubbles prevent the successful realization of the traditional self – healing mechanisms. In this regard, they are undesired!

However, these observations have at the same time inspired the possibility of utilizing air bubble generation in narrow gaps to cause drastic water permeation reduction. In systems where water flow is desired to be stopped /reduced immediately, approaches that utilize the air bubble generation mechanism could be a perfect solution.

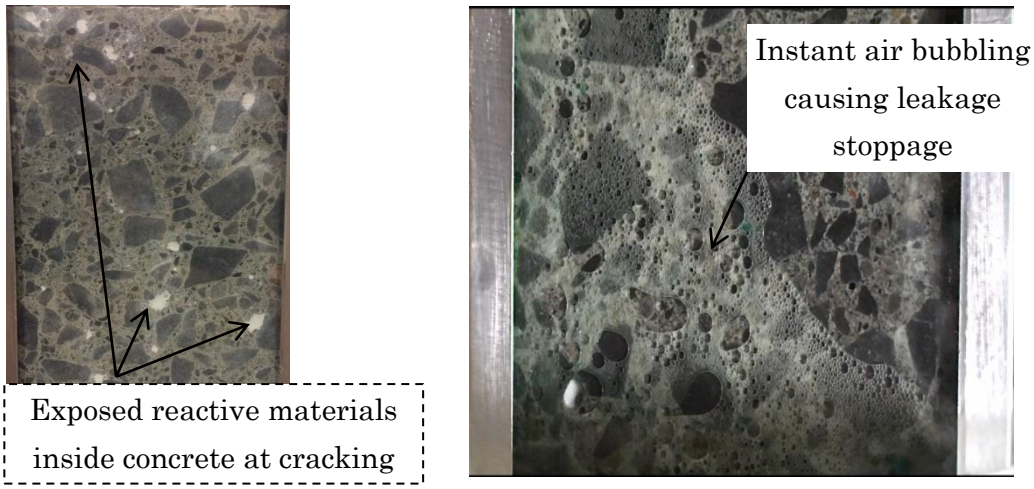


Figure 3-18: The possibility of utilizing air bubble generation technique to instantly stop water leakage in concrete cracks.

In this research, attempt has been made to fabricate a technique that could realize this possibility. It involves fabricating ingredients that release gas when in contact with water, and incorporating them into concrete. Two separate granulated materials would be homogenously added to concrete. In the event cracking, followed by water permeation, water would help to initiate the dissolution of granular ingredients and their reaction would cause gas release within the narrow crack gaps. Once this occurs, water flow should drastically be stopped. Figure 3-18 shows trial expects experiments of the possibility of utilizing this method for water flow reduction

Although this looks like a plausible approach for instant water flow reduction, it should be noted that it does not lead to the actual self-healing that would be beneficial in the long run. It would only serve as a temporary and instant fix for the water leakage problem.

3.10 Chapter summary

In chapter, the origin of investigations of the air bubble phenomena has been clarified and deeply discussed. Air bubble formation within concrete cracks or narrow gaps of water mimics the water flow reduction due to self-healing mechanisms. In closed cracks, observations of these air bubbles cannot be visualized, hence the adoption of a direct visual observation approach for water flow tests. With this approach air bubble creation and eventual growth can be observed and tracked; and at the same time water flow measurements performed. This method is a modification of the water pass test to introduce an observation glass / acryl surface.

Apart from concrete, air bubbles have in the past been observed in porous sandy media during water permeation tests, and in water treatment facilities that utilize stone media for water treatment. In these cases, the effect of air bubbles has been noticed but not greatly investigated. It has been associated with supersaturated water.

The scope of air bubbles observed in these phenomena have been differentiated from already and highly studied categories of air bubbles such as in cavitation, boiling or degassing.

The quantitative effect of this phenomenon has been investigated and discussed. The effect of air bubble growth on water reduction is quantified, and the effect of initial specimen conditions discussed.

Also, the water flow testing method for self-healing concrete testing has been reviewed,

and a modified method proposed. Conditions to be considered for this modification have been discussed, including considering an adequate starting crack width for self-healing testing.

Finally, effort has been made to discuss the implication of air bubbles in concrete cracks and their relationship with water flow. An approach of utilizing this phenomenon in a positive way has been proposed.

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Chapter 4 Co-existence of air bubbles and water flow

This chapter explores and clarifies on the observation of air bubble stability despite the condition of continuous water flow over them. Air bubbles seem to behave as air sieves, de-airing water as it passes over them. It also points out that this is only true for hinged/fixed air bubbles.

4.1 Anomaly of air bubble observation in water flow

The existence of air bubbles in bulk standing water is a known phenomenon; and so is the existence of micro and nano air bubbles in bulk moving water, with the bubbles moving along with the water. This research is founded on the observation of physically hinged air bubbles in the path of water flow, in narrow gaps. This is the anomaly, and is not usually expected to occur. The expectation is that, flowing water would wash out any air bubbles formed within the crack gaps. From observations, the air bubbles start small, about a few microns big and initially fixed on one side of water flow (concrete or any porous material) and then starts to increase in size by taking in more air from water. Throughout this period of growth, water is continuously flowing over the air bubble. The anomaly here is that large air bubbles could be created within fine gaps, and grows to be of millimeter sizes while in the path of water flow! Why doesn't it get washed out, at the very least?

In recent years, there is plenty of research coming up against previous understanding that air micro and nano air bubbles cannot exist in water due to the ideal conditions necessary to create and maintain them. Borkent et al studied the presence and stability of nano-micro bubbles, and referred to them as 'super stable' [1], [2]. With the advance in imaging techniques in the recent years, other researchers have been able to confirm the existence and stability of air bubbles [3], [4], [5], [6]. Others have already explored possible applications such as in ground water bioremediation [7].

4.2 Water flow profiles in narrow gaps with large air bubbles

Any obstacle that comes into the path of water-flow changes the flow profile in a way. Likewise, air bubble growth in narrow gaps changes the water flow profile, and in a gradual manner. Since they start out small and grow large, air bubbles change the surface characteristics of the flow area. In the absence of air bubbles, water flow profiles are observed to be straight and parallel to each. Figure 4-1 shows the difference of water flow profiles with and without air bubbles. In the presence of air bubbles, and since they can't flushed out by flowing water, air bubbles divert water flow direction. While still

maintaining laminar flow condition, streamlines narrow down.

At the base of air bubbles that fully block flow paths, slight turbulence is observed, plus the occurrence of vortices (as shown in Figure.4-1). It is the stability of air bubbles in the path of water flow that changes the flow profiles.

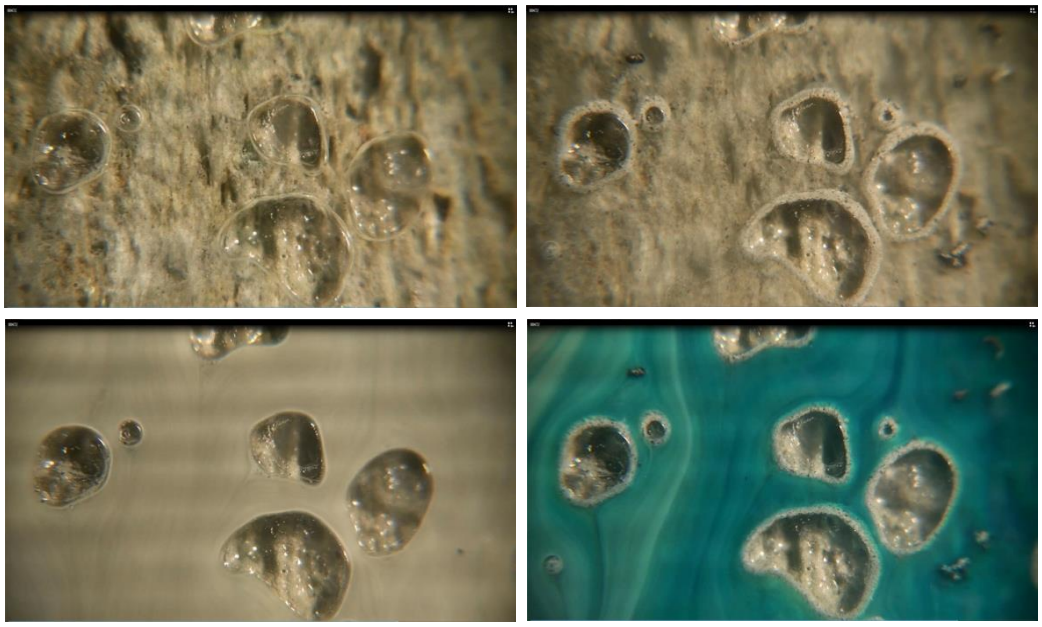

Figure 4-1: Evolution of water flow streamlines in the presence of air bubble stretching between two parallel interfaces (glass and pumice). In the coloured picture (bottom right) the laminar nature of flow lines can be observed.

4.3 Stability of air bubbles in narrow gaps of water flow

The main reasons why air bubbles may be a nuisance in microfluidic systems is because they tend to remain strongly held to the walls of the systems. They do not behave like air bubbles in bulk water, and buoyancy does not play a noticeable role to exclude them from the grip they have on the surfaces. Studies [8-12] identify this as the biggest challenge while dealing with them. Plesset *et al* mentions that the stability of an air bubble doesn't only depend on the acceleration of the interface, but also on its velocity [24]. Geometry too plays a role in stabilizing an air bubble since it determines the nature of the streamlines. In cavitation bubbles, some of these effects do not have enough time to develop fully.

4.3.1 Effect of water pressure and flow speed on created air bubbles

Water flow speed in narrow gaps will depend on the applied pressure, plus the relative

sizes of the micro channels. In principle, outflow rate is faster for bigger channels, and leakage becomes a problem. Higher flow speed will not permit considerable growth of air bubbles. Small air bubbles may remain fixed in the dents, but their overall effect will be small on the flow rates. Increasing the hydraulic head serves the same purpose – of flushing out any loosely held air bubbles. This is why, for self-healing tests, starting crack widths of more than 0.3mm are recommended for testing the efficiency of any self-healing approaches, or the use of relatively bigger hydraulic gradients.

Figure 4-2 shows a simplified measurement of water pressures within parallel surfaces separated by 2.5mm gap. The observed outflows at different heights along the specimen conform to the expected static pressures and satisfy the height dependence of hydrostatic water pressure. This means that in smaller channels, there is probably more pressure at the bottom of such a set up. In reality, it's a combination of kinetic pressure and hydrostatic pressure driving the water flow.

Figure 4-3 shows water flow results of different hydraulic gradients. Specimens with a higher hydraulic gradient have faster flowrate compared to those with smaller hydraulic gradients. However, the rate of water flow reduction cannot be explained based on these results alone.

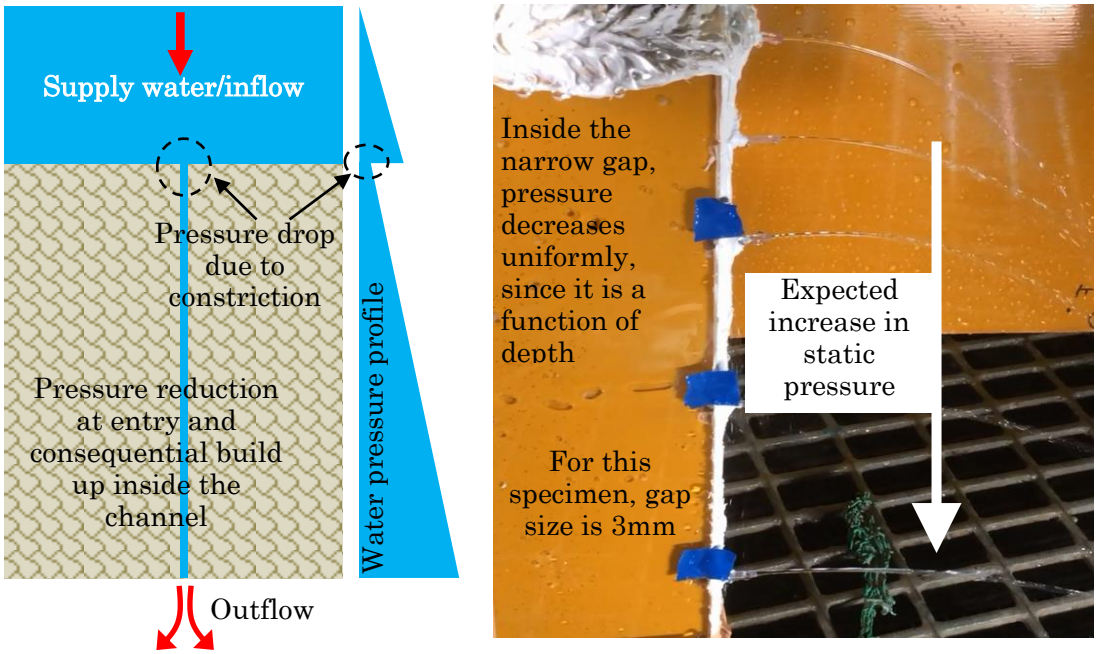

Figure 4-2: A set-up to determine the variation of water pressure within a static narrow gap with water flow for the typical experimental set-up adopted for this research.

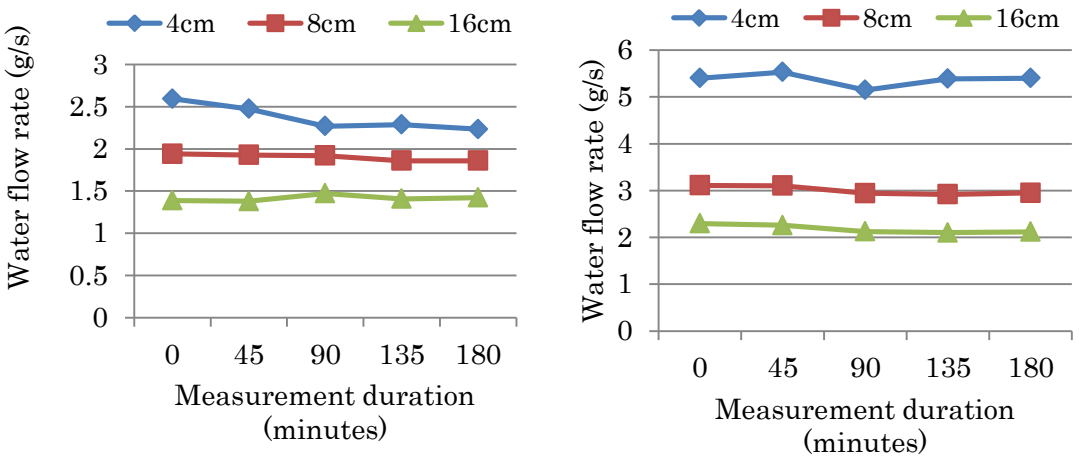

Figure 4-3: Water flow test results for different hydraulic gradients: The hydraulic gradient is doubled for the result in the right graph.

4.3.2 Anchoring of air bubbles

When air bubbles were first observed in cracks with continuous water flow, it was natural to assume that increasing flow speed and water pressure would flush them out. Unfortunately, to a large extent there was no difference. While maintaining water flow, extra water pressure for very small cracks couldn't do much! But of course, without water (for example by turning off the continuous water supply source) anchored air bubbles could be released. The observation revealed an anchoring mechanism of the air bubbles at the dent/surface where they are attached. Extra water pressure could slightly destabilize the position of the bubble, but if strongly anchored, air bubbles cannot be flushed out of the system. Turning off the pressuring water would expose the air bubble to unbalanced pressure, and cause it to burst. But oftentimes, because of the narrow channels, water cannot be completely dried out. Capillary effects ensure that a certain amount of water stays inside the micro channel or crack gap.

In trying to understand anchorage mechanisms, air bubbles could be entrapped in a cavity by water flow [13]. As water moves over a cavity, sizeable air bubbles could be trapped and anchored on the surface of the cavity. In this research, the mechanism of anchorage may initially be similar, but in the long term other mechanisms have to keep the air bubble in place. The role of a nucleation surface and the conditions that exist at this surface must be important in maintaining the bubble in place and potentially growing it in size.

Phan *et al* studies capillary filling in nano-channels and observes the significance of

both the electroviscous effect and the air bubble formation as influence capillary filling in nano-channel [14]. Trapped air utilizes capillarity and dents for anchor, as shown in Figure 4-4.

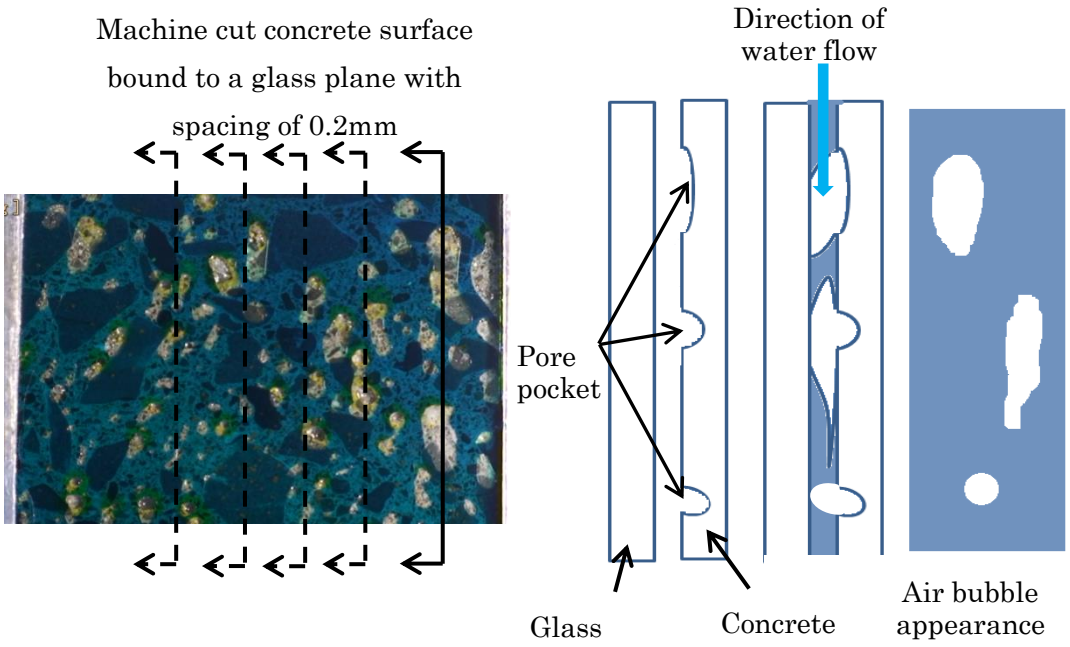

Figure 4-4: Air bubbles formed within narrow gap (left) and a cross-section that reveals possible anchoring mechanism (right).

4.3.3 Capillarity

Capillarity is a very well know mechanism of water rise in thin tubes or slits [14], [15]. The smaller the gap, the higher the capillary forces in water systems. Concrete cracks too quickly take in water by such a force. The attraction between water molecules and any other material (glass, or concrete) will determine how high up the water rises. If air bubbles exist in the narrow slits, capillary forces will keep them intact. Figure.4-5 illustrates effect of capillary in presence of air bubbles in narrow gaps. In relatively large gaps like used in these experiments (0.1 ~ 0.2mm), the effect of capillarity is not so significant, though noticeable. Even after water flow has been cut, a given lower section of the specimen can still maintain water held within the interfaces; and if air bubbles were initially anchored, they will remain in place until the water dries out. It is expected that in much smaller channels, the effect of capillarity is much bigger.

In order to achieve air bubble stability within such narrow gaps, capillarity plays a role in keeping water within the gap. Capillary works along with surface tension, and also

dependent on the nature of the material. Most experiments or demonstration of capillary effect tend to use the same materials, such as a glass tube; in this research consideration was made for the concrete – glass gap. As such, calculations of capillary forces or capillary rise, would have to consider the differences in contact angle for the two surfaces.

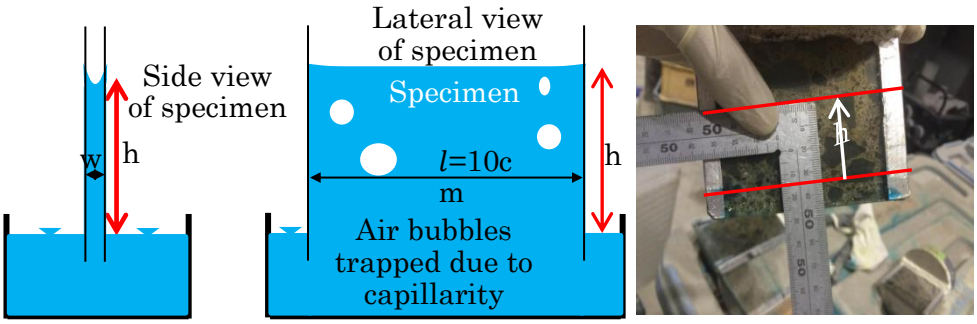

Figure 4-5: Investigation of capillary rise in narrow interfaces with water flow with already grown air bubbles.

4.3.4 Effect of gap size on air bubble growth

Full air bubble growth means that the air bubble has grown to cover the entire gap of water flow. In this case it would cause water flow blocking. Before an air bubble is covering the entire gap width, it's mainly causing water flow braking. Once the bubble reaches to the opposite side of the gap, it starts growing parallel to water flow and in a radiating format. It attempts to maintain a circular or oval shape stretched in the direction of flow, as illustrated in Figure 4-6.

The smaller the gap size, the easier it is for the bubble to connect on the opposite end. Once there, it attaches and gains more stability. Also, smaller gaps imply low speeds of water flow, providing adequate condition for quicker growth.

The effect of gap size, w, on air bubble growth is such that it affects how fast the bubble anchors onto the other side of the parallel surfaces. The bigger the gap size, the longer and harder it for air bubble growth. This also implies a high level of instability due to faster flow rate.

Ushida *et al* measured flow properties of nanobubble mixtures passing through micro-orifices and found that channels with less than 50 micro had significant effect on flow properties (pressure drops) [16]. This difference in flow properties using nano bubble water was however attributed to factors like slip wall, interfacial tension and others. It is also possible that the different micro-orifice size permitted nano bubble behaviour to

occur to different extents.

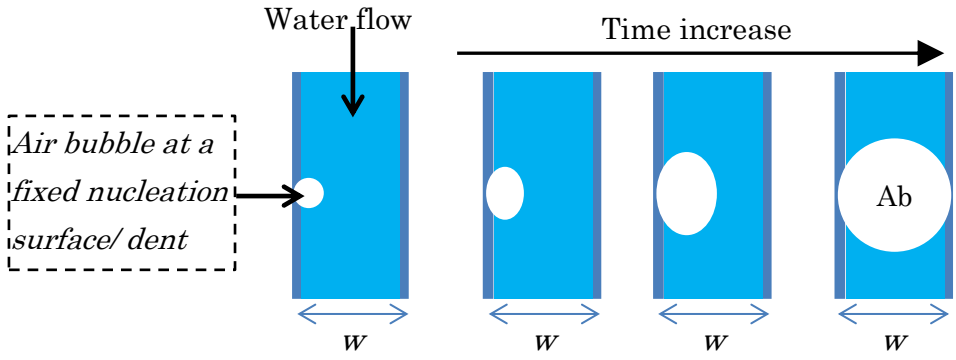

Figure 4-6: Understanding air bubble growth and the effect of the gap size on growing bubble

The effect of gap size, w, on air bubble growth is such that it affects how fast the bubble anchors onto the other side of the parallel surfaces. The bigger the gap size, the longer and harder it for air bubble growth. This also implies a high level of instability due to faster flow rate.

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In reality, and based on observations, the effects of these mechanism are much more significant for smaller scale systems. Like it is already known, these effects are irrelevant in bulk water, or even for relatively sizeable confinements of water. However, if we narrow down the scale of observation to the nano and sub-micro sizes, the effect of size and relevance of the air – water interface become quite significant and cannot be underestimated.

Moreover, because of the stability these smaller interfaces provide, via capillarity and un-flushing effect of flow water, air bubbles tend to have a higher residence time compared to larger dimensions.

4.4 Effect of de-aired water and tap water

Water naturally contains air, and it's possible for us to remove some of the air contained in water, for example through vacuuming or boiling. Once this happens, we end up with

de-aired water. De-aired water is not water containing zero amount of air, but rather having air saturation levels of about 1 – 2 mg/L of dissolved oxygen [17]. In our research, de –aired water containing about 3 – 5 mg/L could be achieved, and this defines the meaning of de-aired water in this research. De-aired water is incapable of causing air bubble growth, at least air bubbles in the observable range of our experimental set-up.

Tap water is usually pressurized and contains supersaturated levels of air content, more 100%. This type of water quickly leads to air bubble evolution [18]. Once opened up to atmospheric pressure, for example in a bucket, dissolved air content in tap water quickly diminishes. This is the usual observation when we put it in a glass, it will form air bubbles on the sides of the container in which it is put. Other bubbles will form at the bottom and quickly escape out as soon as they start growing in size. Equilibrium saturation levels have to be attained according to Henry's gas absorption law (see section 3.6.1). Figure 4-7 shows the effect of effect of using tap water and de-aired water for a standard specimen (concrete bound to glass with 0.2mm gap). On the left is a specimen with fully grown air bubbles as a result of using tap water, and on the right is the same specimen supplied with de-aired water and undergoing reverse air bubble growth.

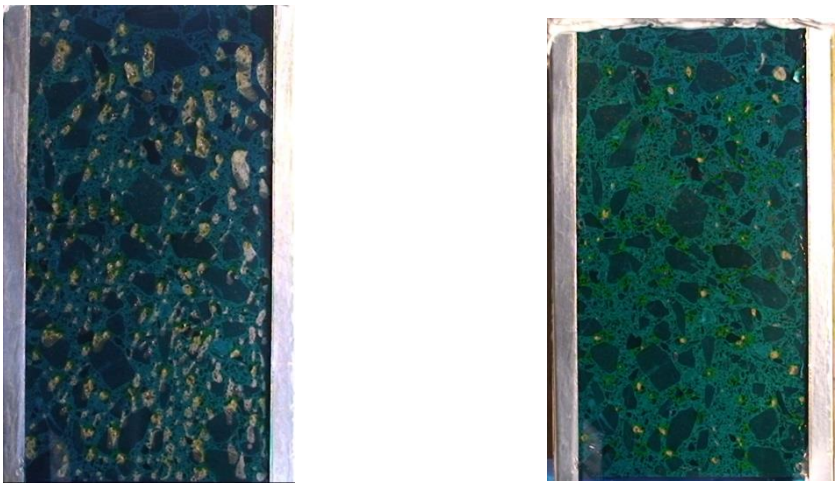

Figure 4-7: Effect of using tap water (left) and de-aired water (right) on the same standard specimen for the same duration.

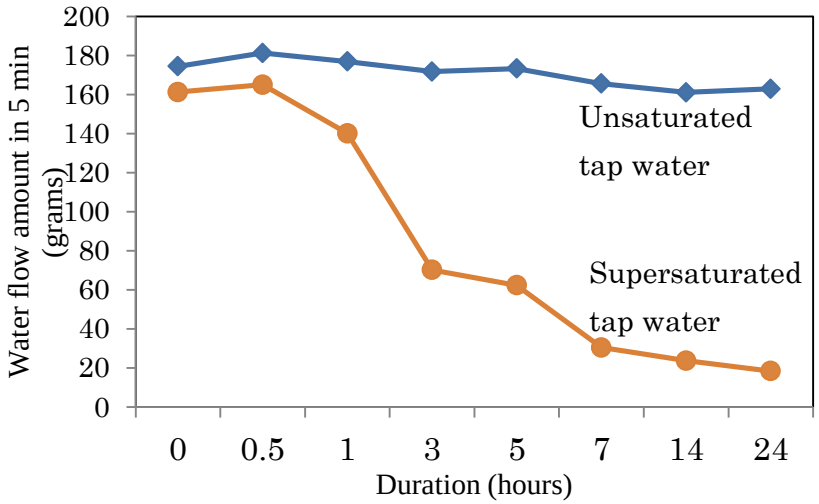

Figure 4-8: Water flow duration graphs showing difference of de- aired (unsaturated water) and supersaturated tap water, for the same specimen.

In order to understand the co-existence of air bubbles and water flow, these two types of water were used initially in order to understand the origin of air bubbles (tap water and de-aired water). Figure 4-8 shows the water flow – duration graph for a concrete specimen supplied with tap water. Water flow reduction is noted and is thought to be due to the effect of air bubble growth. In the same figure, the water flow test was performed for a standard specimen with unsaturated water (de-aired water). It now becomes clear, the effect of the two waters with different air saturation levels. Air bubbles seize to exist in the presence of flowing de-aired water (also refer to section 5.1).

Table 4-1: Variation of dissolved air content with temperature and pressure

Temp °C	Pressure of air above the water in atmospheres							
	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00
	Concentration of air dissolved in water in mg/L							
0	37.27	74.55	111.82	149.09	186.37	223.64	260.92	298.19
5	33.00	65.99	98.99	131.99	164.98	197.98	230.97	263.97
10	29.33	58.66	87.99	117.32	146.65	175.98	205.31	234.64
15	26.53	53.06	79.58	106.11	132.64	159.17	185.69	212.22
20	24.25	48.50	72.75	97.00	121.25	145.50	169.75	194.00
25	22.36	44.73	67.09	89.46	111.82	134.19	156.55	178.91
30	20.88	41.77	62.65	83.54	104.42	125.31	146.19	167.08
40	18.51	37.02	55.53	74.03	92.54	111.05	129.56	148.07
50	17.02	34.04	51.06	68.09	85.11	102.13	119.15	136.17
60	15.94	31.89	47.83	63.77	79.71	95.66	111.60	127.54
80	15.05	30.10	45.15	60.20	75.24	90.29	105.34	120.39
100	15.05	30.10	45.15	60.20	75.24	90.29	105.34	120.39

All concentrations are in mg/L. 1 atm = 101.325 kPa = 101.325 kN/m^2 = 1.013 bar.

Table 4-1 shows the concentration of dissolved air at several temperatures and

pressures. There is a known and well understood explanation for the nature of the values in the table, and how they relate with our observations in experiments with air evolution from water.

4.5 Effect of pH of flowing water on air bubble growth

Air bubble growth means that either of two things is happening: 1) the gas in the bubble is expanding or 2) more air is entering the bubble. In this research, expansion is ruled out. It hypothesized that bubble growth occurs by letting in more air across the air – water interface. This mechanism creates an expanding interface.

According to several researchers [19], [20], [21], and [22] the air water interfacial properties could be influenced by the pH of the solution. Based on this, alkaline and acidic water types were prepared and used for water flow tests involving air bubble growth. The alkaline water was obtained by mixing a solution of sodium hydroxide with water to attain a pH of 10; and the acidic water was by mixing hydrochloric acid in water to attain a pH of 4. These solutions were maintained at dissolved air saturation contents of below 100%. Figure 4-9 shows the set-up for this test. Both water flow tests showed reducing water flow rates with time, and for the alkaline water, flow stabilized after 75 minutes of continuous water supply as seen in Figure 4-10. The acidic water test continued to show decreasing water flow values, even beyond 75 minutes of the test. At 90 minutes, several air bubbles were observed to be growing in the test set-up for acidic water as shown in Figure 4-11. Probably the growing air bubbles could explain the continuingly plummeting water flow values that were measured. The mechanisms of water flow rate reduction in the case of alkaline water and a section of acidic water test are clearly discussed in Chapter 6.

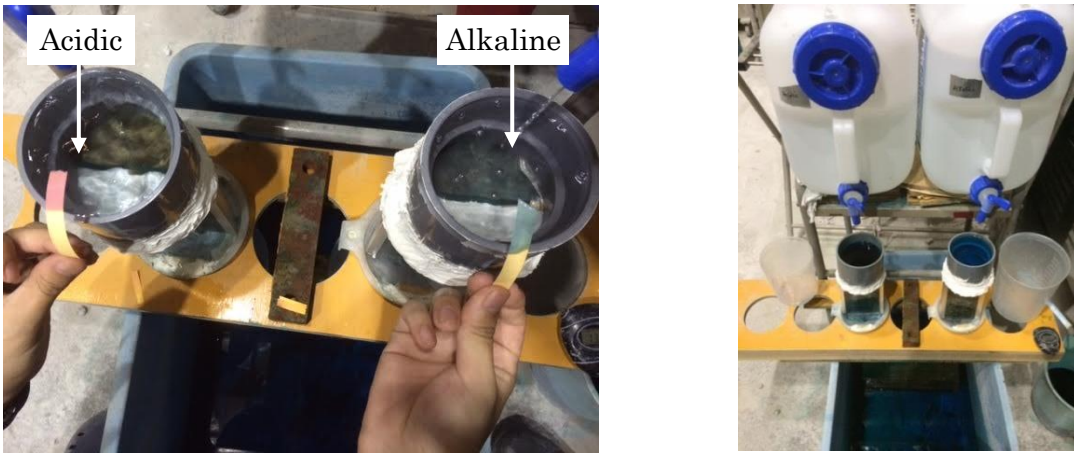

Figure 4-9: Water flow tests with alkaline and acidic water

The effect of pH of flowing water on air bubble growth is linked to the potential charge at the air – water interface [23].

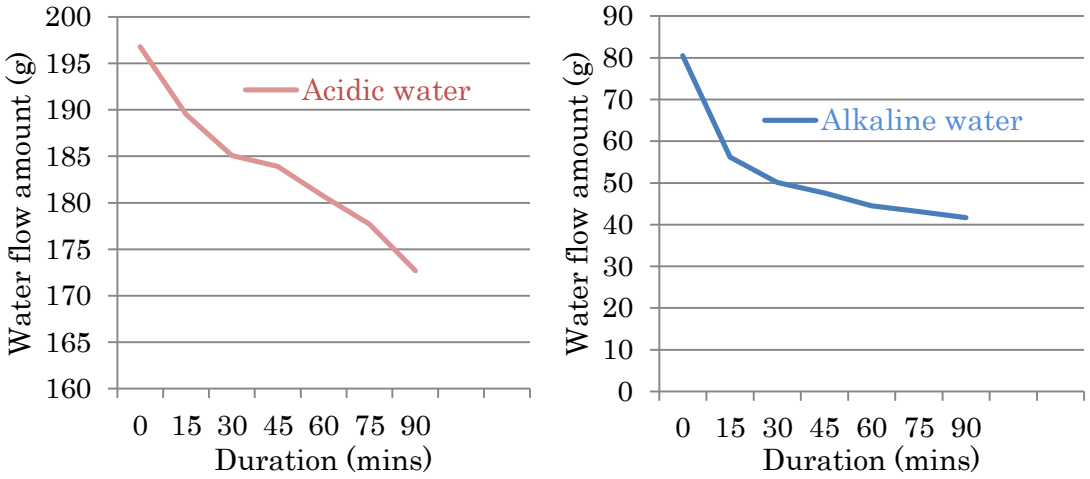

Figure 4-10: Apparatus for water permeability tests, adopted by Nishiwaki et al., 2014, for self-healing testing of concrete specimens [23]

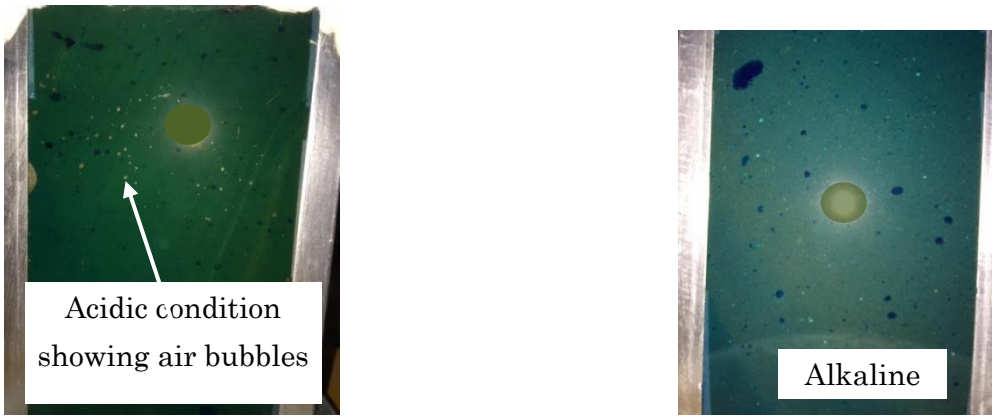

Figure 4-11: Specimens that were exposed water flow tests with different pH values of water. On the left, is acidic water showing small air bubble growth and on the right, for the alkaline set-up.

The effect of pH on water flow reduction cannot clearly be explained in these results, and this is because of the difficulty in understanding how pH affects water at a molecular level. What is clear is that surface tension of water can be affected by changes in pH and this occurs at a molecular; if this happens, water flow properties could be changed and thus affect water flow rates. Figure 4-12 shows the variation of pH with surface tension, and the generalized understanding of surface tension by Beattie *et al* (2014).

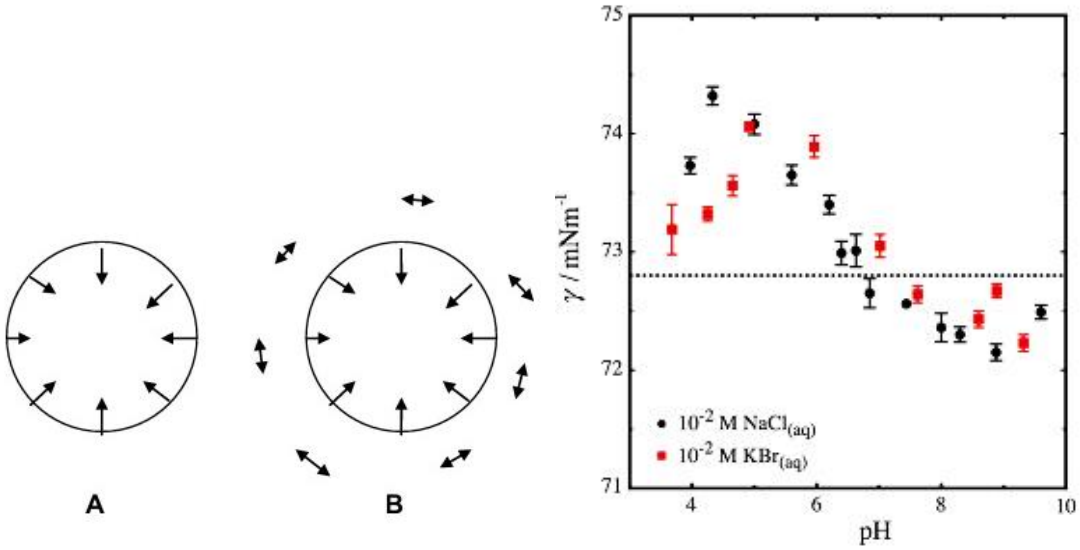

Figure 4-12: Conventional view of surface tension without (A) and with (B) surfactants, and the measured surface tension variation with monovalent salts at 10mM concentrations and 273 K [19]

It should be noted that for concrete specimen, and probably for most specimens, contact with acid solutions may initiate reactions that may affect observations and measurements. Concrete which is made up compounds of carbonate could react with acid to give off Carbondioxide or water vapour as byproducts. These could for example explain the small air bubbles that develop in the specimen exposed to dilute acidic conditions of water flow. Figure 4-9 shows water flow tests being conducted with acidic and alkaline water supply conditions.

4.6 Vacuuming and specimen water saturation technique

In order to rid the specimens of any initially contained air and to prepare de-aired water, vacuum soaking of specimens and vacuuming of normal water are done. In this technique, the specimens to be used for water flow tests are placed in a container containing water, and this is put in a vacuum set-up and negative pressure applied. This procedure ensures that most of the air contained in the specimens is driven out by a suction process. Figure 4-13 shows a typical vacuuming set-up for specimen preparation.

Similarly, to ensure that the water used in the process is 'air-free', de-aired water too is prepared in the same way.

The purpose of this procedure is to further strengthen our understanding that air

bubble growth benefits from the contained in water and not what's probably coming from the micro-pore structure of concrete or any other test material. It is for the same reason why materials such as Aluminium are used, to further verify the origin of air for bubble growth.

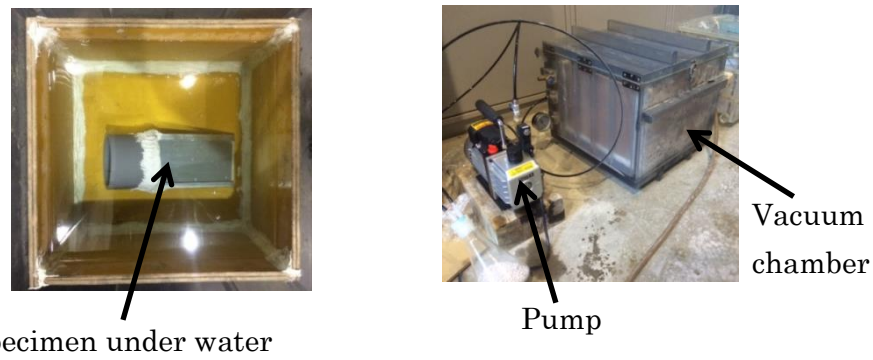

Figure 4-13: Specimen preparation by vacuuming soaking to get rid of internally trapped air and also to saturate specimen with water.

4.7 Bubble rise in narrow interfaces.

In bulk water, air bubbles once formed could easily detach from their nucleation point and rise out of the water. Initially, a similar phenomenon was expected for bubbles formed in narrow gaps as well. But in most cases the opposite was observed. There was no burping taking place in the system with fully grown air bubbles, and air bubbles were continuously held between the walls of the parallel surfaces. Only those small enough, and under low water flow speed, could rise out of the narrow gap. At higher speeds of water flow, the small loosely held air bubbles get washed out instead!

To investigate this further, an experiment was designed to try and understand why this was the case. In this experiment, using a similar specimen set-up, air bubbles were injected into the narrow gap using a syringe. Figures 4-14 and 4-15 show an illustration of the set-up. On injection, air bubbles are observed to rise out through the water. On their way up, size increases. This is similar to air bubble rise mechanisms observed elsewhere [25], [26]. The reducing water pressure is the explanation for this increase in bubble size.

These air bubbles rise smoothly through the water, but the moment they touch the walls of the glass or other material, they are immediately slowed down.

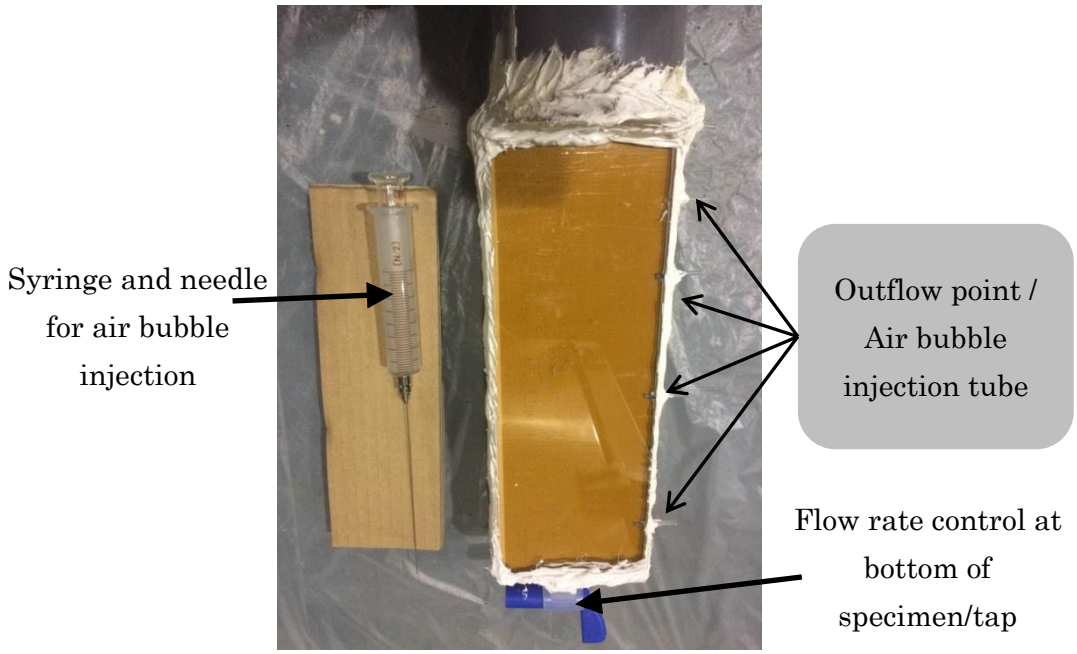

Figure 4-14: Specimen set-up to determine air bubble rise through narrow gaps with stagnant or moving water flow.

Legendre *et al* compared Carbondioxide and air bubbles rising through water in which case the CO_2 was dissolved into water during the rise through the two-meter column. The air bubbles could rise through the water unaffected.

Brown [26] proposed a mechanism and model of flow considering bubbles moving through stagnant liquids in a tube. It accounts for the effect of liquid viscosity on the flow in the film around the bubble.

Most of the experiments involving bubble rise or bubble movements in narrow gaps are performed for relatively large liquid columns. Taylor flow or Taylor bubbles for example considers elongated gas bubbles flowing along in capillary channels and almost occupying a bigger cross section of the channel [27]. A thin liquid film exists to separate the bubble from the wall

Wang and Tong have investigated the deformations and oscillations of a single bubble rising through a narrow vertical tube by numerical models [28]. Of interest to their research are the bubble oscillations during the rise, which they attribute to surface tension. Even their research considers relative large air bubbles (20mm), much smaller bubbles have been studied in our research (< 2mm). Bubble oscillatory motion was observed especially for the bubbles that make through the channel.

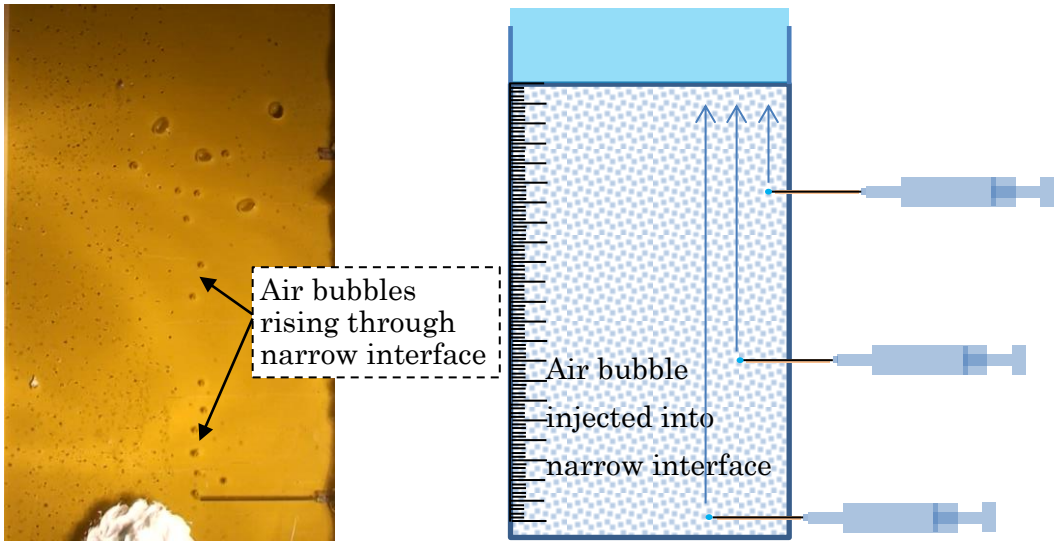

Figure 4-15: Air bubbles inject between two walls separated by a gap of 3mm. Some air bubbles rise out of the liquid column while others are trapped on the wall of the channel where they stay fixed.

4.8 Chapter summary

In this chapter, the question of why air bubbles stay anchored within the narrow gaps has been tackled. Right from the start, and by the mechanisms of formation, micro and nano air bubbles defy theory! They however continue to grow and stay fixed at their nucleation points/surfaces by the favorable conditions narrow gaps of water flow provide. High capillarity potential of narrow interfaces ensures that water is always bounding the trapped air bubbles; the interconnection that exists by the surface topology within narrow gaps also ensures that bubbles can be hinged at more than one place. In addition, the continued supply of air – rich water feeds the bubbles or sustains the equilibrium conditions within the narrow gaps. From literature we also find that the shape and water streamlines play a role in ensuring small air bubble survive through their infancy.

In extreme cases of high speed water flow, the anchoring forces can easily be overcome and air bubbles get washed out of water. More still, unsaturated water flow conditions work to reverse the air bubble growth mechanisms and cause dissolution of the air back into the air-deficient water.

Unlike in most literature where bubble rise through water columns has been largely studied, similar experiments performed for much small water columns (between interfaces) air bubble rise is not easily possible; only those bubbles small enough

manage to escape through the gap. This observation is natural given the relative size implications in the two investigations.

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Chapter 5 Air bubble growth observations and necessary conditions

This chapter covers the investigations into the necessary conditions for air bubble growth. The direct mechanisms favoring air entry into a fixed air bubble within a narrow gap with water flow. It also provides a basic understanding of the characteristic of air bubbles, such as interfacial surface properties.

5.1 Reverse air bubble growth

In order ascertain the origin of air bubbles and to understand the mechanism of their growth, several parameters were adjusted. Initially, air bubbles were observed to increase in size, implying there was air exchange from the water and into the bubble, across the interface. The biggest concern was whether this could be reversed, to open doors in the opposite direction. As mentioned in section 4.4, the use of flowing de-aired water on already grown air bubbles causes them to size down and completely diminish. Air bubble growth alone is an anomaly, especially since it is envisaged to start from smaller and finer air bubbles whose existence shouldn't happen, theoretically [1].

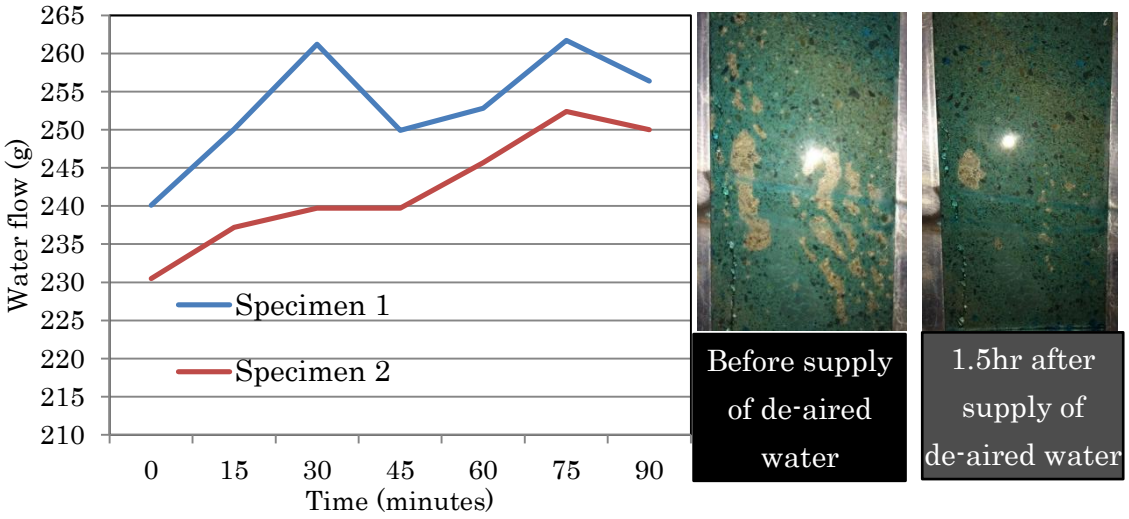


Figure 5-1: Water flow tests starting with a specimen with visible air cavities, and then supplying unsaturated water (left); on the right are images of before and 1.5hours after supply of water.

To investigate this further, specimens initially supplied with supersaturated tap water and thus with grown air bubbles, were then supplied with vacuum treated de-aired water. Air bubbles were observed to shrink in size until they disappeared out of the

narrow gaps as can be seen in Figure 5-1. In cavitation, once bubbles have been formed in bulk water, they are quickly pressed in by surface tension and disappear within less than a second [2]. This is totally different to what was observed. The rate of air bubble disappearance was observed to be faster than same size air bubble growth, though. This could be attributed to the difference in corresponding levels of air saturation away from the equilibrium. For example, would 120% and 80% dissolved air content saturation at standard temperature and pressure cause the same rate of size change in both directions? In the reverse air bubbling experiments, de-aired water of 65 – 75% dissolved air saturation was used, and yet slightly over 100% tap water was used to cause air bubble growth in 24 hours. The air bubbles formed in 24 hours could easily be diminished by de-aired water within 4 hours. The dissolved air saturation potential could be the driving force for the observed difference in bubble growth and reverse growth mechanisms.

Reverse air bubble growth is also proof of actual air bubble growth. The air bubble behaves like an elastic membrane capable of changing dimensions by simply taking in air from water or putting it back. To be able to do something like that, it implies that the air bubble attains a significant level of stability within the narrow gap. Video recording and observations reveal that an air bubble in the path of water flow maintains its anchorage position to within 1mm of movement and also depending on the existing conditions, such as speed of water flow and static and dynamic pressure of flowing water.

5.2 Determining the surface charge of micro bubbles in water

It is possible that the surface charge of air bubbles influences its interaction with the surroundings [3], [4], [5]. In this research, it was attempted to study the behaviour of micro gas bubbles formed between two parallel and oppositely charged plates. Air bubbles were generated by electrolysis of a dilute solution of sodium chloride. From literature, it was suggested that the air – water interface is negatively charged [6], [7], and [8]. It was therefore expected that hydrogen gas bubbles formed at the negative terminal of the electrolysis set-up would move towards the positively charged plate. The gas bubbles would move as negatively charged particles. What was observed was as depicted in Figures 5-2 and 5-3.

Since the set-up is carried out in bulk environment, air bubbles are at the same time acted upon by the buoyancy force, forcing them to rise out of water. The electrostatic pull and buoyancy force causes a resultant direction of movement of the micro gas

bubbles towards the positively charged plate. The distance between the two charged plates dictates the speed and resultant direction. Only gas bubbles generated at the negatively charged plate were observed to move towards the positively charged plate. In reality oxygen gas bubbles were also being produced at the positive plate. These bubbles only rose out of the solution slowly. Figure 5-4 shows the actual set-up used for these tests.

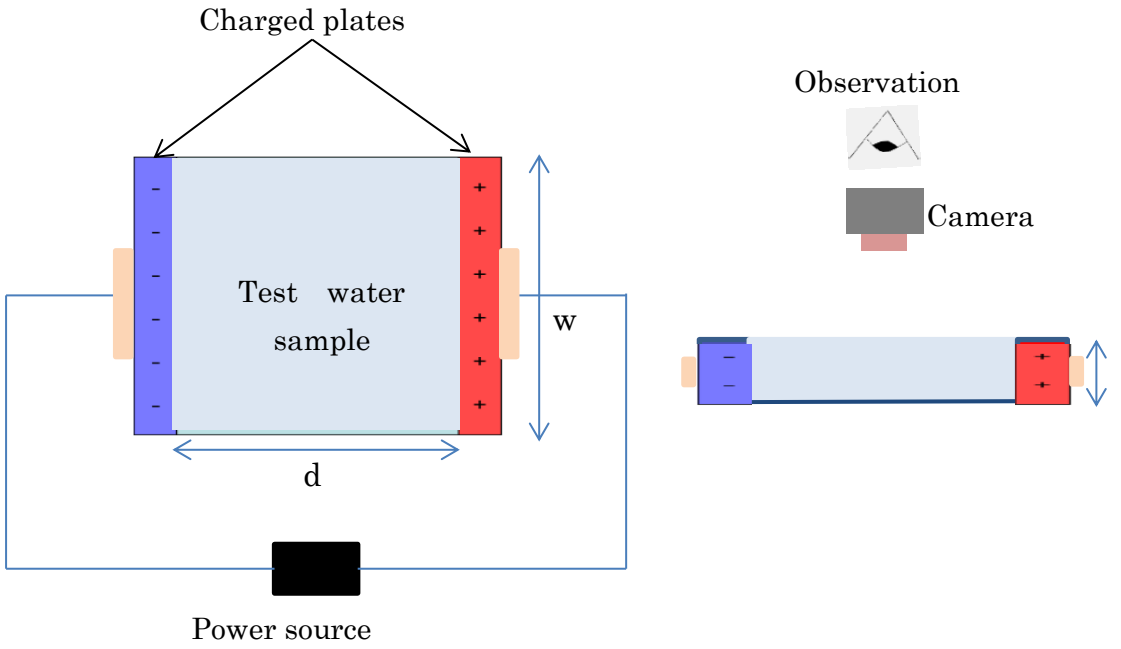


Figure 5-2: Illustration of set-up to investigate the effect of charged plates on air bubbles in water. Submillimeter size air bubbles could be investigated under this set-up, and the effect of bubbles having charge investigated.

Through this indirect approach, the air bubble surface charge could be linked with what has been reported or suggested in some of the literature – that it's negatively charged, that's why negatively charged air bubbles move towards the positively charged plate. The possible drawback of our approach could be the low voltage potential on the charged plates, of up to 35 volts, compared to what some literatures report on using (several kV as seen in Figure 5-5). The air bubble lifetime during this observation is also short, since air bubbles are rising out of solution at the same time.

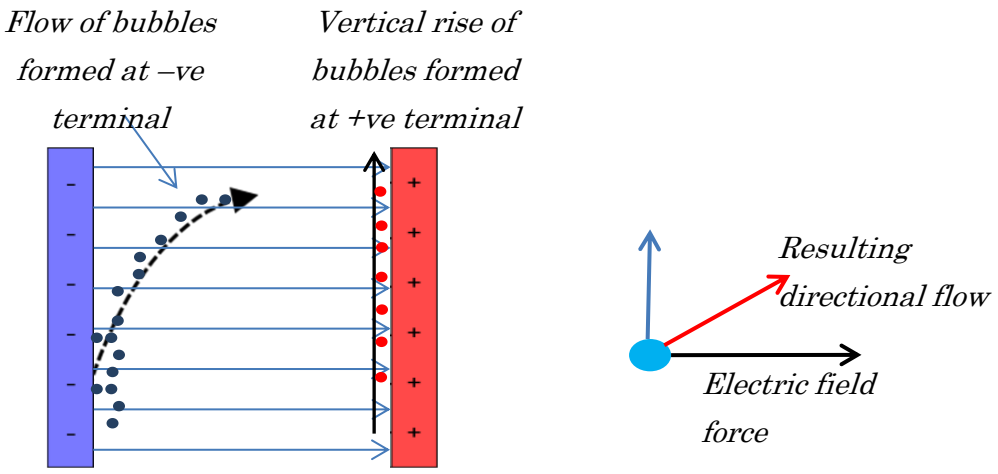


Figure 5-3: Schematic representation of the observation when air bubbles are generated within water and between two oppositely charged voltage plates.

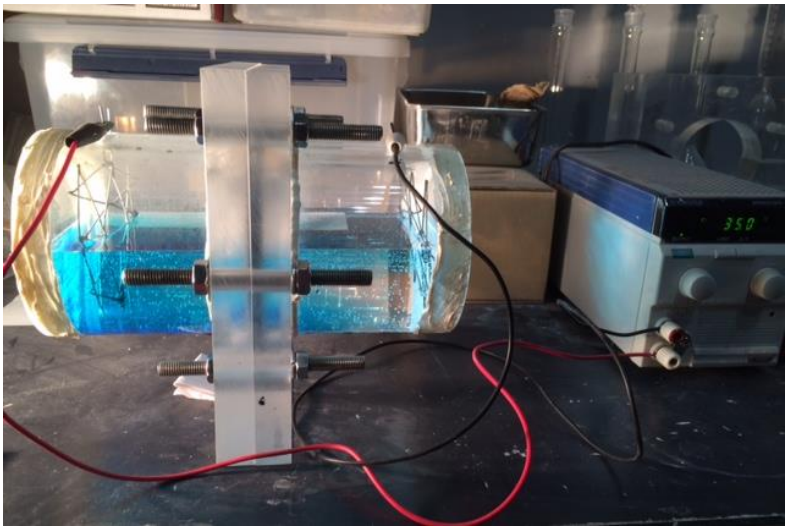


Figure 5-4: Actual set-up to study air bubble movement between charged plates in water.

The accuracy of this set up and observations could at a molecular level be constrained by the ionic solutions, or much so be aided by the polar nature of water. Migration of favourable ions due to a voltage potential could possibly cause micro and nano bubble movement in the same direction. Although the observations seem to support earlier assertions that air bubble surfaces are negatively charged, further considerations needs to be made

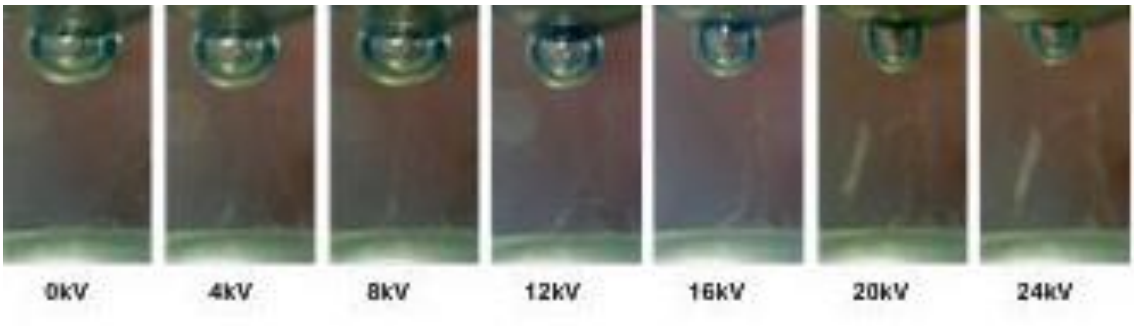


Figure 5-5: Effect of different electrostatic voltages on a static air bubble created at a spherical surface. Bubble deformation could be observed with higher electrostatic voltages (Talaat et al, 2012) [9]

5.3 Mechanisms of air bubble growth

Air exchange occurs at the air – water interface. The actual mechanism of gaseous molecules crossing over from water into the gaseous phase (still surrounded by water) is still not yet clear. However, the conditions that facilitate this phenomenon have been studied and largely understood in this research. There is plenty of research attempting to understand the growth of gas bubbles, especially from a nucleation point of view [10], [11]. In cavitation dynamics, bubbles grow starting at a nuclei and reach considerable high internal pressures and maximum size beyond equilibrium [12]. They then become unstable and collapse-in on themselves with release of a significant amount of energy (heat and sound). In this research, this kind of bubble growth that happens within such short time intervals is not observed. What is however observed, and within the narrow gaps is that bubbles start small, and continue to increase in size for as long as water flow continues and stability is in place. The duration of growth is in minutes to days.

5.3.1 Conditions necessary for air bubble growth

Three of the conditions necessary to accelerate or act to reverse the air bubble growth mechanisms are mentioned here. Existence of a nucleation point, Water movement around air bubble, and air supersaturation in water are discussed here.

5.3.2 Effect of porous nature of concrete

The porous nature of concrete provides nucleation sites for air bubble attachment and growth, within the narrow gaps of water flow. This is one of the main reasons why concrete cracks are a good candidature to study or observe this phenomenon. Small pores and dents on the crack surface of concrete or any material are points of low energy requirement for phase change. In narrow gaps, they are points where air bubbles are

formed and fixed against water flow. Figure 5-6 shows an illustration and relevance of nucleation points.

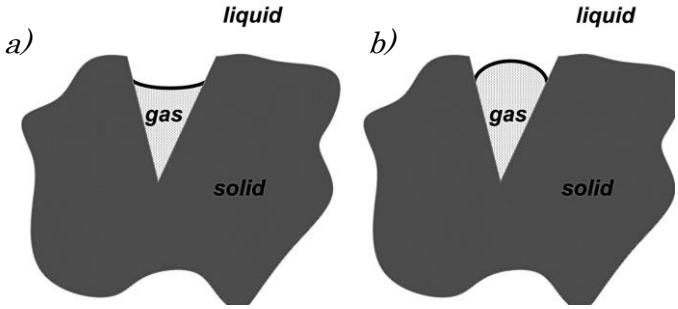


Figure 5-6: The crevice model of nucleation: a) Stabilization mechanism of nuclei; b) Nucleus starts to grow into a bubble when the pressure in the surrounding liquid is reduced. (E. A. Brujan, 2011)

Rough surfaces possess a number of these points compared to smoother surfaces. Water flow tests were performed for glass – glass parallel plates to further understand air bubble growth. No air bubble growth was observed for the glass – glass specimens. On the contrary, significant air bubble growth was observed for glass – concrete, glass – wood, and other rougher surfaces. Figure 5-7 shows the result of more than 12 hours of water supply.

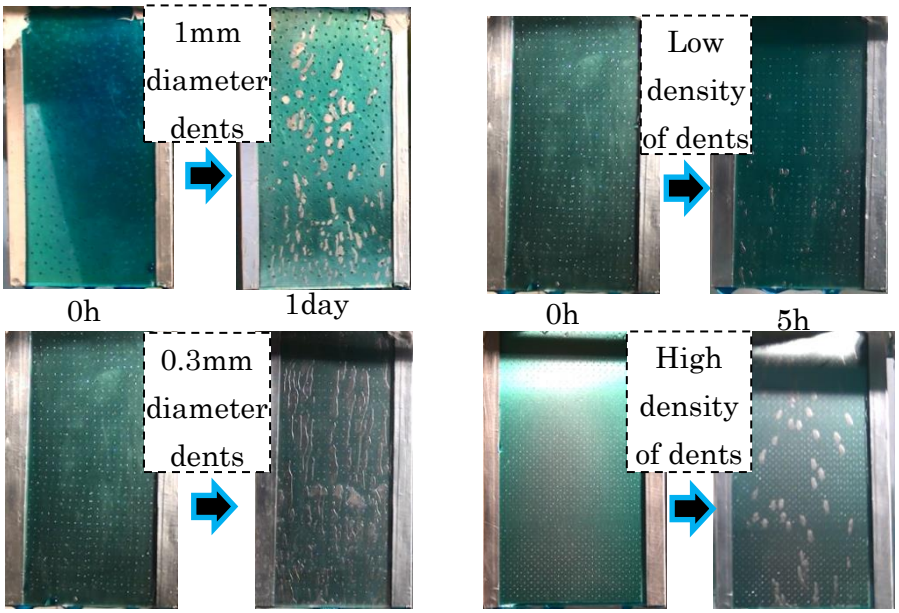


Figure 5-7: Air bubble growth observations with aluminium plates having different dent sizes and dent density. Effect of dent characteristics on air bubble growth is studied by varying size of nucleation point and density of nucleation points.

5.3.3 Water movement

For air bubble growth, movement of water around the interface is necessary. It is this air movement that continuously brings in air-rich water and takes away de-aired water. In order to investigate the effect of water flow, two set-ups were prepared. One involved a growing air bubble that was placed in static water, and the other set-up exposed to continuous water flow. For the same time, the air bubble in static water did not change in size, while the one exposed to continuous water flow continued to grow. Figure 5-8 shows the results of the two set-ups.

In this research observations are made for water flow in narrow parallel surfaces. One side of the parallel surfaces is glass, and the other is the study material. The dynamics of water movement in these narrow parallel planes is determined by water pressure head, capillarity, material surface characteristics, and the flowing liquid characteristics (temperature, viscosity, etc.).

The illustration of the contributory mechanism of water flow is illustrated in Figure 5-9 Fresh flowing water continuously replenishes air-deficient water at the interface [13]. Even if we have supersaturated water, without water flow, air bubble growth is inhibited

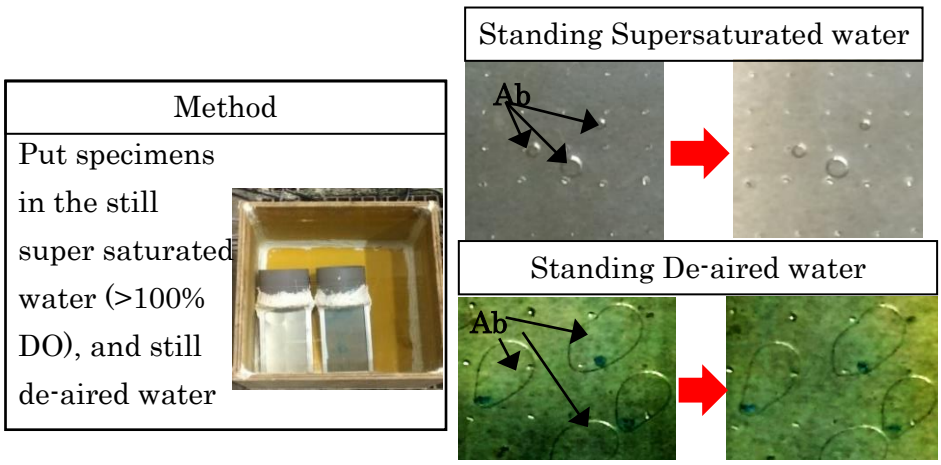
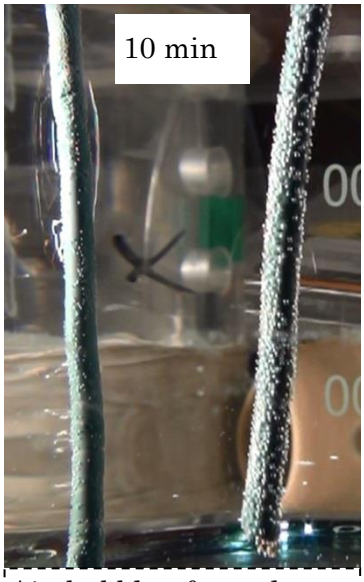


Figure 5-8: The effect of the requirement of flowing water for air bubble growth is investigated using specimens with small air bubbles and or fully grown ones in still supersaturated or de-aired water.

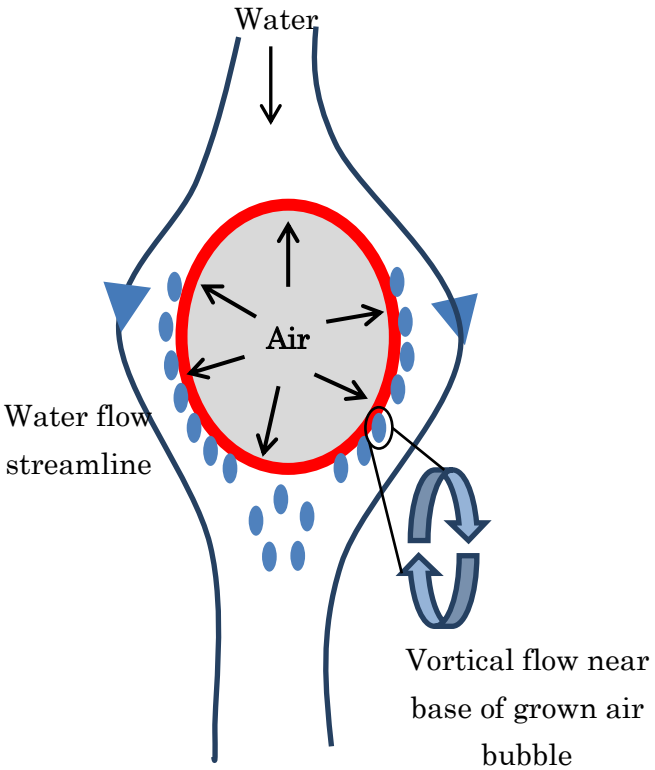
Investigations into the relevance of water flow were the premise of this research. Therefore understanding water flow in narrow spaces is believed to be the key to combating water ingress related deterioration mechanisms in concrete. Its ability to cause air bubbles to grow in narrow gaps is therefore when supersaturated water is

flowing reveals more of the mechanisms involved.

In reality, and based on observations, water flow is a necessary condition for air bubble growth. Although in this research, only water flow speed developed for gaps sizes of standard specimens of 0.1 – 0.2 mm was investigated, the effect slower speed that occurs in much finer gaps such as concrete micro pore structure needs to be investigated. Slower speed of flow would ensure stable conditions for air bubbles, and probably enable an efficient air withdraw from the surrounding water. Too fast and the air is not fully removed from the water by the anchored/fixed air bubble.



Air bubbles formed on a nucleation surface that is continuously moved through standing water (right), and one left to stand still in the same water



Schematic of Air bubble – water interface

Figure 5-9: Water movement acts to bring air-rich water to the interface while at the same time take away de-aired water away from the interface. It is either water movement over the bubble or bubble movement through the water.

Water agitation effects on the kinetics of air absorption by water are studied by Apostolos [24]. The air mass transfer coefficient was found to depend on the mixing energy per unit water volume, as well as the ambient temperature and pressure.

5.3.4 Water supersaturation

It is not only flowing water that's necessary, its dissolved air content plays a bigger role

in the mechanisms of air bubble growth. Supersaturated water contains more air than it would at equilibrium conditions [12]. Supplying this type of water in a set-up with air bubble growth contributes air to the growing bubble. To verify this, measurements of dissolved oxygen content were used as a representative figure for the percentage of air saturation content in water. Tap water had more dissolved air than any other type of water. It is also relevant to note that dissolved air in water contains a higher oxygen concentration (36%) than what is in the air (21%). Water saturation is influenced by ambient temperatures and pressure, and the saturation rate determines the direction of gaseous diffusion at the air – water interface.

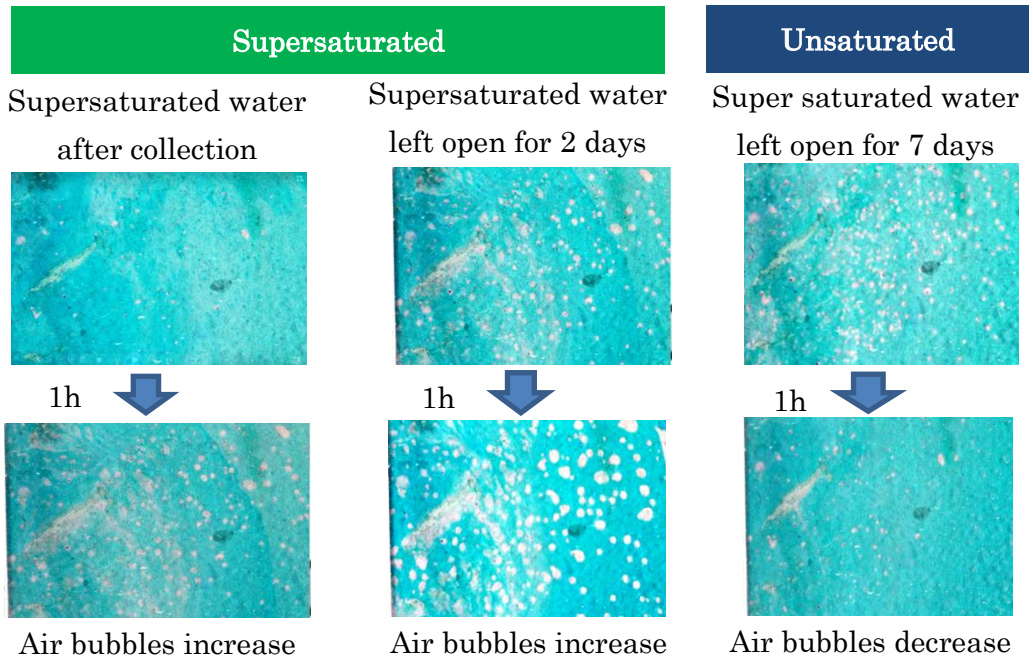


Figure 5-10: Air bubbles subjected to different water types (supersaturated and unsaturated) and observing whether air bubbles grow or disappear, under water flowing conditions.

The three conditions (existence of a dent, super saturation, and water movement) in their oneness cannot cause air bubble growth (see Figure 5-10). It rather takes a combined effort of them all to contribute to air bubble growth. It is currently understood that these are only accelerating conditions for this phenomenon, and that there is possibly the nature of the air – water interface, that under such narrow conditions of water flow, causes air to form bubbles. It is still not clear the origin of these bubbles, whether they are nucleated from micro and nano air bubbles already present in supply water [14] [15], or are birthed from the dissolved molecular air in water.

5.4 Equilibrated dissolved air content for water flow tests.

There is an equilibrium point for air saturation in water at standard conditions of temperature and pressure. At this point, water is 100% saturated. Below this, it is unsaturated and above is supersaturated. In this research, water flow tests investigating the effect of another specific condition on water flow were performed with water having equilibrated dissolved air content (98 – 100%). To achieve this saturation level, a micro bubble blower is lowered into a container of water while it stands for hours. Micro bubbles are formed and cause perturbations in water, helping to come out with most of the excess dissolved air content. This is true for supersaturated waters. Dissolved air content levels (DO) are measured from time to time to check saturations. It takes about 3 – 4 hours to equilibrate 20 litres of tap water at 20°C in the laboratory. Figure 5-11 shows some of the water flow tests using equilibrated water.

Water flow results obtained by using equilibrated water generally show limited effects of dissolved air compared to those by tap water. However, if the measuring duration is narrowed down to within the first two hours, both water flow show reducing water flows with time. This observation is further discussed in chapter 6.

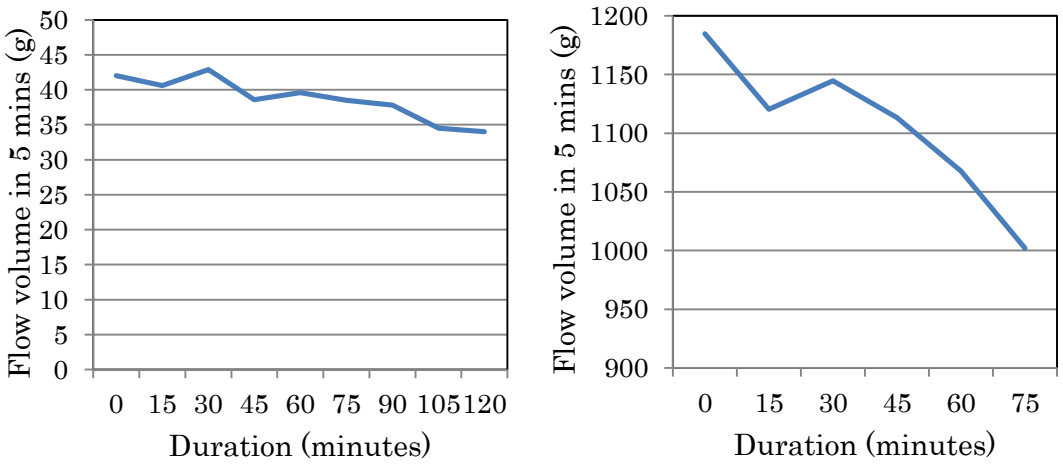


Figure 5-11: Water flow test results using equilibrated water (<100% dissolved oxygen content). Water flow reduction tendency is still observed.

5.5 Seasonal variation of dissolved air and its effect on water flows

As the natural seasons vary, so do the temperatures outside. This directly affects conditions in the real environment. Amount of dissolved air is temperature dependent [12]. In places where four seasons exist, the differences in season can be observed in

terms of changes in dissolved oxygen content, and in turn, water flow test results become different for every season.

In this particular research, carried out in Japan, with four unique seasons, their effect was studied. For every 15th of the month, starting August 2015, tap water was collected and dissolved air content measured, plus the water temperature, as shown in Figure 5-12. Similar water was then used to perform water flow tests on a standard specimen within 24 hours. 10 litres of the water were then kept for continuous monitoring of DO (dissolved oxygen) content in the laboratory.

Tap water is pumped at higher pressures and usually contains more dissolved air than it would at the same temperatures. Also, dissolved air saturation rate is dependent on the saturation potential, which is influenced by the ambient pressure and temperature. Exposing the tap water to an open environment would help to equilibrate the dissolved air saturation according to Henrys law.

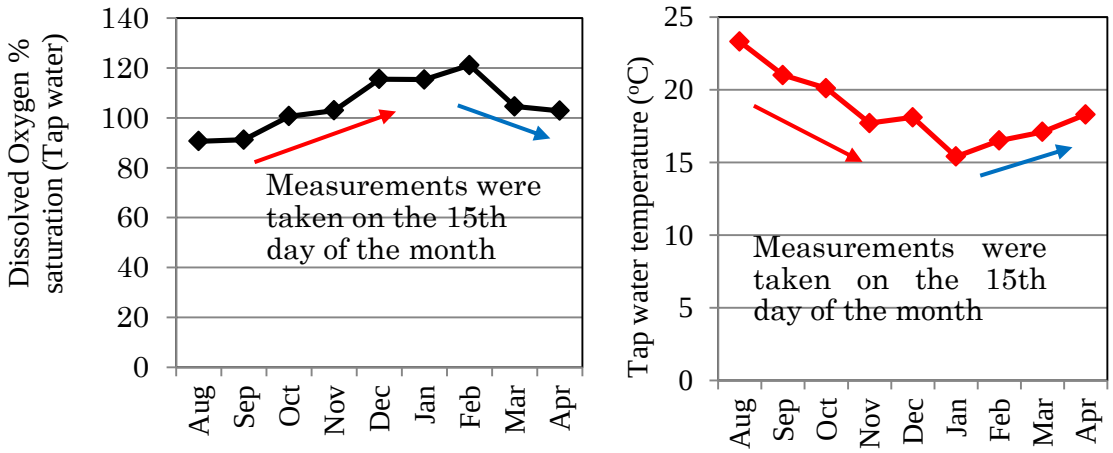


Figure 5-12: Results of dissolved oxygen measurements over a period of 9 months (left), and their corresponding water temperatures over the same period. Measurements are taken on the 15th day of the month.

Figure 5-12 shows the dissolved oxygen variation for 8 months starting August. The observation follows a natural and expected trend. Higher temperatures lead to lower DO content, and vice versa. If this monthly water is used to perform water flow tests, results vary according to the amount of dissolved air. Figure 5-13 shows the water flow results using the monthly collected water. There is a negative correlation between dissolved air content and water flow values. The effect of dissolved air on water flows is directly associated with the ease of formation of air bubbles that cause water flow

reduction.

It was found that, self-healing concrete water flow tests performed in winter always exhibited faster water flow reduction tendencies compared to tests done in summer. Before the understanding of the air bubble phenomenon, results of winter tests could easily be taken to be superior to others. It is now clear, the effect temperature changes. Tap comes directly from the mains, and there is almost no control on its temperature, except as dictated by the surroundings of the environment it goes through. Depending on the dissolved air content, equilibrium levels corresponding to lab conditions (20°C) can only be attained after more than 24 hours. In winter, it would take about 7 days to achieve equilibrium air saturation for tap water in the laboratory.

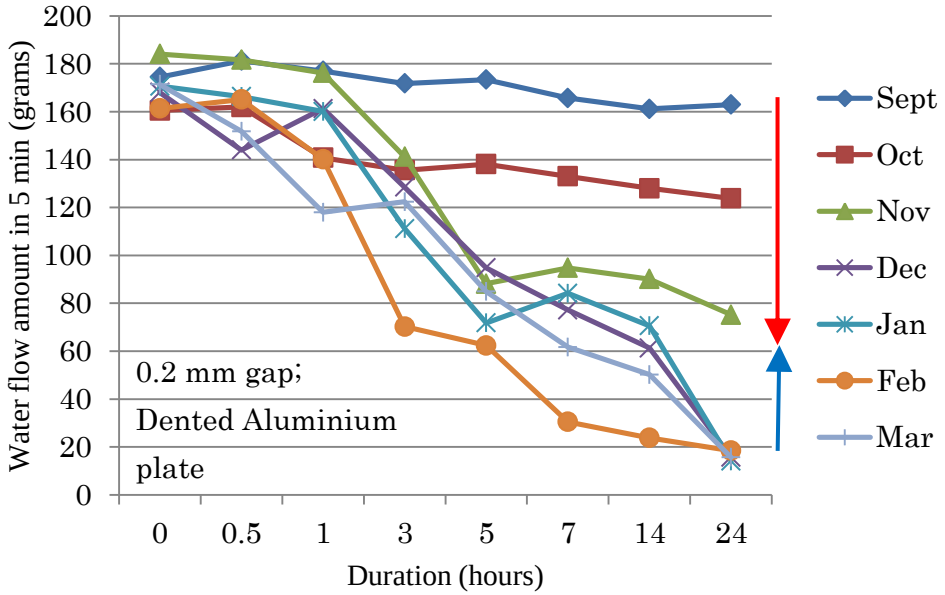


Figure 5-13: Water flow test results using water collect on the 15th of every month, from September – March, using a single standard specimen for all tests.

5.6 Effect of ultrasonic waves on air bubble creation and growth

Conditions necessary for air bubble growth have been clearly understood, and they are all mostly accelerating factors for air entry via the air – water interface. Ultrasonic cavitation occurs when water is exposed to ultrasonic waves [16]. Micro and nano air bubbles are quickly formed in a bulk medium with ultrasonic waves [17]. This same principle is used in degassing of liquids.

In this study, we wanted to understand the effect of ultrasonic vibrations on an already

existing air bubble. The experiment was first performed in a bulk water container as shown in Figure 5-14. Exposure to ultrasonic waves immediately creates air bubbles; these stay 'suspended' in water, and vibrating about as is illustrated in Figure 5-15. This movement (vibration) is believed to simulate water flow around the air – water interface and provide the necessary condition of water movement for air bubble growth.

Ultrasonic pulses act to move the air bubble about a certain fixed position. This is similar to water flow over the air bubble surface. What an air bubble needs to grow is air-rich water in the immediate surrounding, and the existence of a pressure difference to drive the air from water and into the bubble. It is possible that ultrasonic pulse could vibrate the air – water interface and probably accelerate air flow in the preferred direction of equilibrium for the system.

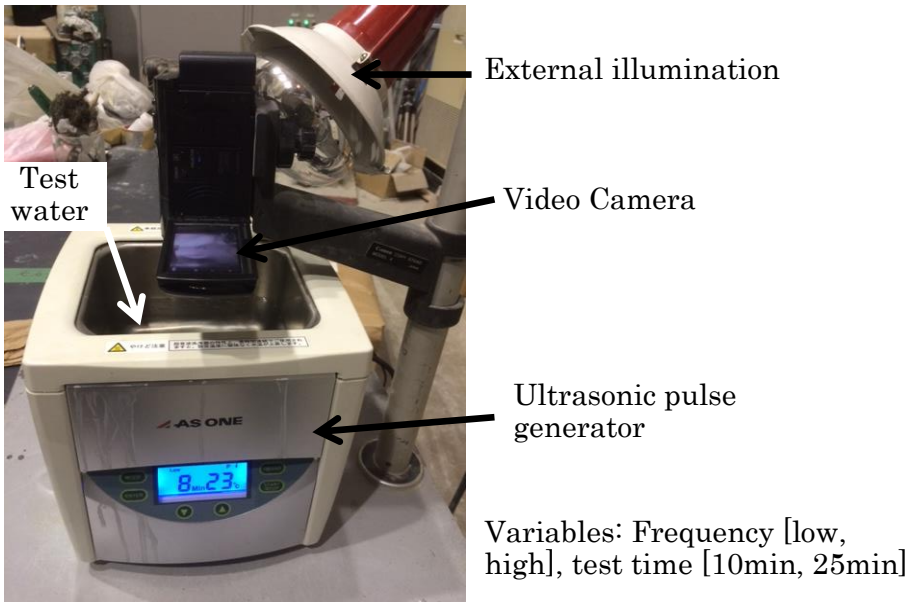


Figure 5-14: Set-up to investigate the effect of ultrasonic pulses on air bubbles, and air bubble growth.

Figure 5-14 shows the adopted set-up to investigate effect of ultrasonic waves. It is not exactly clear how ultrasonic waves would affect a fixed air bubble in a narrow gap with water flow. It would be interesting to investigate this effect with a more suited ultrasonic waves producing device. The effect of ultrasonic waves on a static air bubble in a narrow gap would be interesting to study.

To further understand the effect of ultrasonic waves, de-aired water, alkaline and acidic water were used. With de-aired water, there was no significant cavitation bubbles formed in the bulk water. This is probably expected, since the water is air deficient. The

same observation was made for alkaline and acidic water.

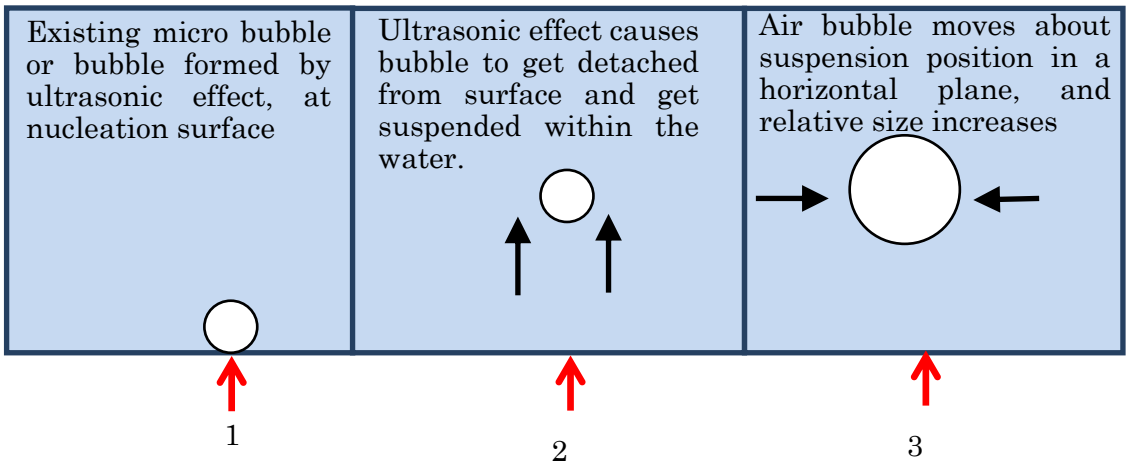


Figure 5-15: Observed effect of subjecting air bubbles to ultrasonic pulses in a bulk container. Bubble motion and eventual size increase could be observed during a vibrating motion.

5.7 Effect of magnetic force on air bubbles

Magnets have a magnetic field around them. It was anticipated that since air bubbles are charged, a magnetic field would have an impact on them. A magnetic field distorts the shape of the air bubble, and the presence of inertia forces destroys parabolic growth [9]. Some researchers also reported that a rotating magnetic field may lead to an increase in air bubble diameter [18]. Deformation of the equilibrium shape of the liquid water interface is likely for air bubbles under a magnetic field [19]. In some literature, bubble growth may be slow under the influence of magnetic field. Figure 5-16 shows the effects of different electromagnetic voltages on static air bubbles on a spherical head.

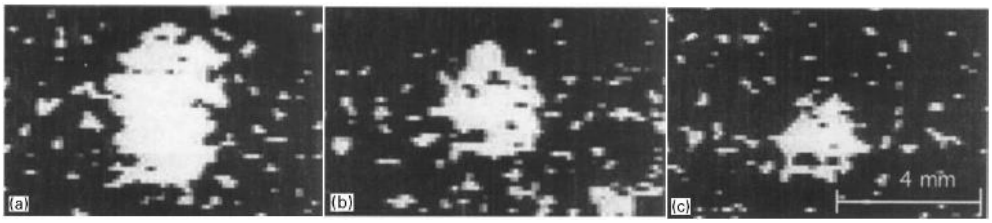


Figure 5-16: Analyzed images of air bubbles released from a tube from the bottom of a cell, with different applied magnetic field strengths and showing different deformation extent as they rise through a cell set-up. (Nakatsuka et al, 1999) [29]

In this research, the effect of magnetism was not clearly understood and investigated, but it's possible that a magnetic field could interact with the possibly charged surface of

the fixed air bubbles in narrow gaps. From the literature and about the characteristics of air bubbles, such as having charged surfaces, it is expected that there would be some effect on a fixed air bubble in the pressure of a magnetic field. The extent of the effect would largely depend on the size of the bubble and the strength of the magnetic field. Deeper investigations of the effect of magnetic fields on air bubble growth within narrow gaps of surface is recommended.

5.8 Effect of different material surfaces

One of the prerequisites of air bubble growth is the existence of a nucleation surface such as a pore on concrete surface, or a dent or a crevice. As such, different materials were investigated to check if a similar phenomenon could be observed. Materials with different micro-pore structure, grain structure, or surface roughness were investigated and compared. Wood, concrete, pumice, Styrofoam, plane glass, plane and dented Aluminium plates were used in this experiment for mainly comparison. A plane Aluminium is dented with 0.1 – 0.2mm diameter depressions to produce a surface representative of unique surface pore structure of concrete. This dented Aluminium plate; along with machine cut concrete surfaces are used to most of the tests in this research. It was initially thought that possibly air trapped in concrete could contribute to this air bubble growth, that's why a fully solid material such as a dented Aluminium plate was opted for in this study.

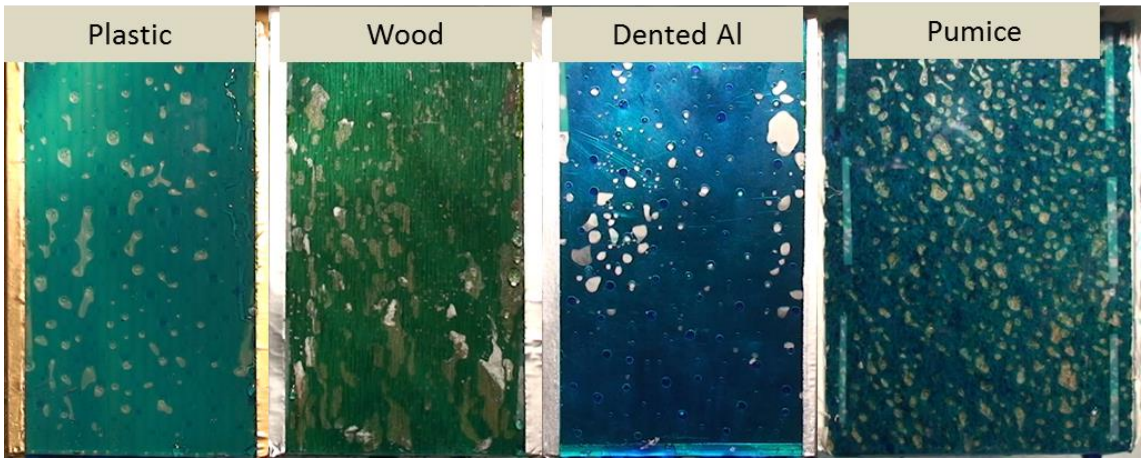


Figure 5-17: Result of water flow observations for different materials. Air bubble growth is observed for any materials with a considerable surface structure capable of having nucleation conditions.

Figure 5-17 shows the results of water flow tests, using supersaturated tap water for the same duration (12 hours). The difference in air bubble growth for the different

materials could be attributed to their surface properties. The spacing was uniform for all specimens. The effect of different material roughness can also be seen when for the same material (Aluminium), different levels of roughness (smooth, smaller dents, bigger dents, denser dents, etc.) produce different effects. Figure 5-18 shows the effect of different dent density for an aluminium plate.

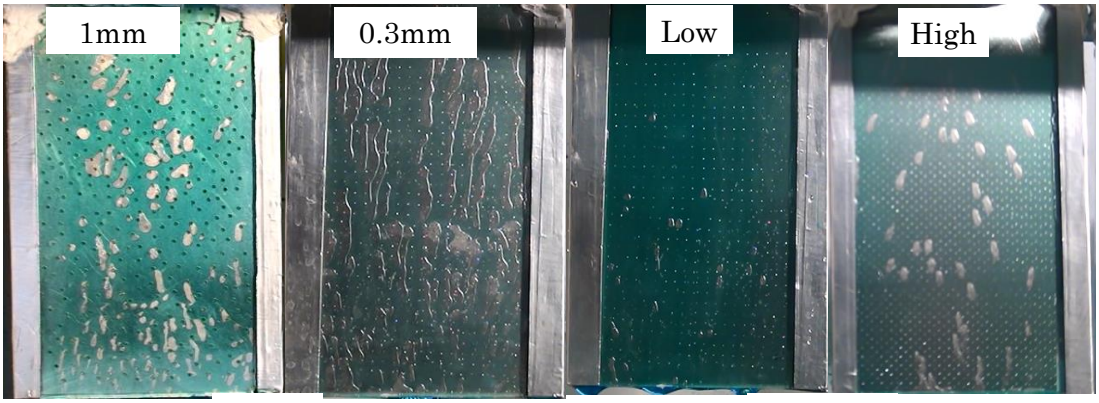


Figure 5-18: Different surface characteristics yield different air bubbles quantities at different rates of growth. Even for the same material, such as aluminium plate, air bubble growth could be different.

The most bearing factor about the effect of different material surfaces is their level of surface imperfections as compared in Figure 5-19. These are what are important for air bubble nucleation, fixation, and eventual growth. Besides this, their level of hydrophilicity or hydrophobicity will determine the liquid – solid interactions in the narrow gaps of flow. The materials used in this study were mostly water loving.

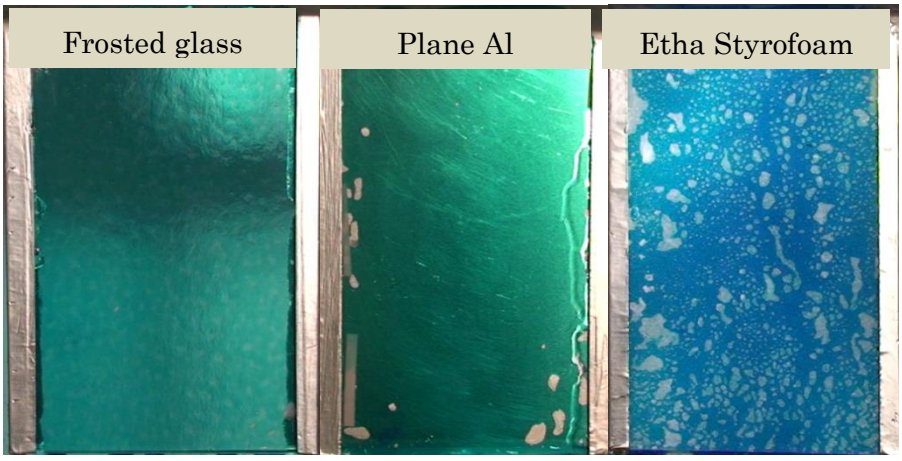


Figure 5-19: Comparison of effect of surface characteristics of different materials such as frosted glass, plane aluminium plate and Styrofoam.

Figure 5-20 shows water flow results that correspond to the observations made for specimens in Figure 5-19.

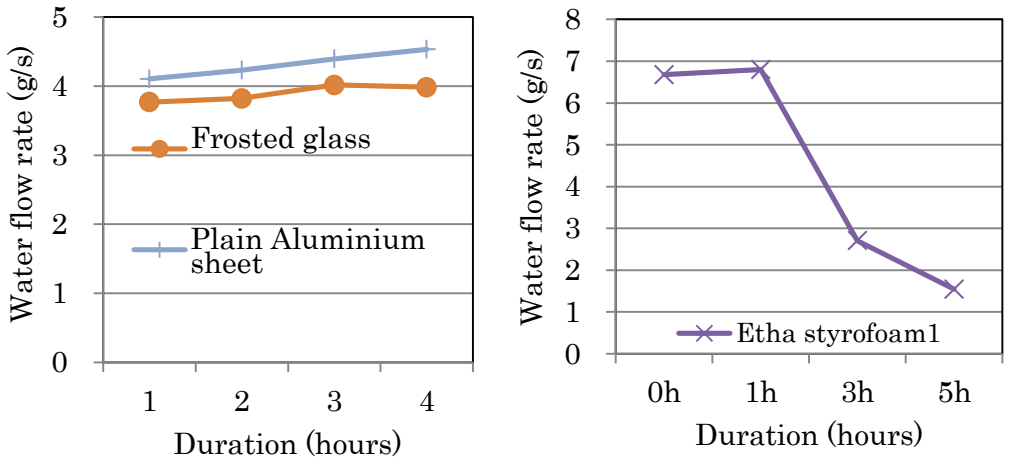


Figure 5-20: Water flow test results for specimens capable of growing air bubbles and those (right), and those with smooth surfaces and thus incapable of developing air bubbles with their narrow interfaces.

Yan *et al* performs numerical simulation of nucleate boiling in micro channels, and considers the effect of surface characteristics in helping to sustain air cavities, which later influence parameters like heat transfer [21]. In heterogeneous nucleation, small gas pockets could be stabilized at crevices or pores found within the path of flow [22-25]. Based on this, it highly likely that surfaces with such pockets would favour stability of micro and nano bubbles and water flow over them would help to supply the necessary air for growth.

The formation mechanisms of air bubbles entrapped into water drops impinging into hydrophobic graphite substrates with different topographies [26] further highlights the stability the topography offers to the air bubbles that are entrapped. In our research, concrete and some of the other surfaces are highly hydrophilic and the conditions of stability could be theoretically more conducive for air bubble entrapment [26].

Studies on the fluid flow patterns reveal the potential of the existence of a turbulent regime to influence the size of and generation of air bubbles [27-29]. By performing image processing of generated bubbles, micro bubble size distribution were performed and compared, plus analyzing the shape of the bubbles.

5.9 Chapter summary

Water flow reduction in narrow gaps such as concrete cracks or interfaces occurs largely due to the presence of air bubbles. The origin of these air bubbles has been found to be the water which flows through the narrow gaps. Their nucleation and continued stay within the interfaces is facilitated by the surface characteristics of the materials out of which the narrow gaps are made. Rougher surfaces encourage growth and attachment of air bubbles, while narrower gaps keep it strong fixed. The amount of dissolved gases in the permeating water plays a larger role in supplying the necessary ingredients for bubble growth. This alone is not enough, water flow should help to remove air-depleted water and replace it with air-rich water at the surface of the air bubble. All these mechanisms take place at the air water interface.

Air bubble growth is not instant, and takes place from within minutes to days, depending on the existing ambient conditions. Once the air bubbles have been formed, they continue to grow until equilibrium conditions of size and stability are attained. Because of their strong anchorage, water flow may not easily wash them out of the narrow gaps. Loosely anchored smaller bubbles may however be washed out. The stable air bubbles will continue to reside in the interfaces for as long as supersaturated water is continuously flowing. Reverse air bubble growth is equally possible, when de-aired water is supplied to a set-up with already grown air bubbles.

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Chapter 6 New understanding of water flow reduction

Water flow reduction mechanisms have continued to evolve with newer understanding from time to time. In self-healing concrete, it was initially thought to be the contribution of several mechanisms (see section 2.1.1), until they were investigated one by one. After this investigation, the cause of the drastic water flow reduction in self-healing concrete tests was found to be the creation of large air bubbles blocking water flow (Ikoma 2014).

This research further clarifies on Ikoma's contribution. This research adds further that, it's not only the large air bubbles that contribute to the drastic water flow reduction, but largely the effect of so many micro and nano air bubbles attached on the dense micro-pore structure of surfaces (concrete surfaces) These small air bubbles work by a totally different mechanism, water flow braking mechanism. Figure... illustrates an evolved understanding of the water flow reduction mechanisms for narrow gaps such as concrete cracks.

6.1 Water flow reduction in absence of air bubbles

Contrary to previous observations of large air bubbles by the naked eye, and associating this with the water flow reduction continuously measured [1], a new observation has been made. Significant water flow reduction has been observed to occur in the absence of any visible air bubbles. If the measurement time is narrowed down from 24 hours, to just within 2 hours, water flow reduction is strongly observed, assuming all other factors are constant.

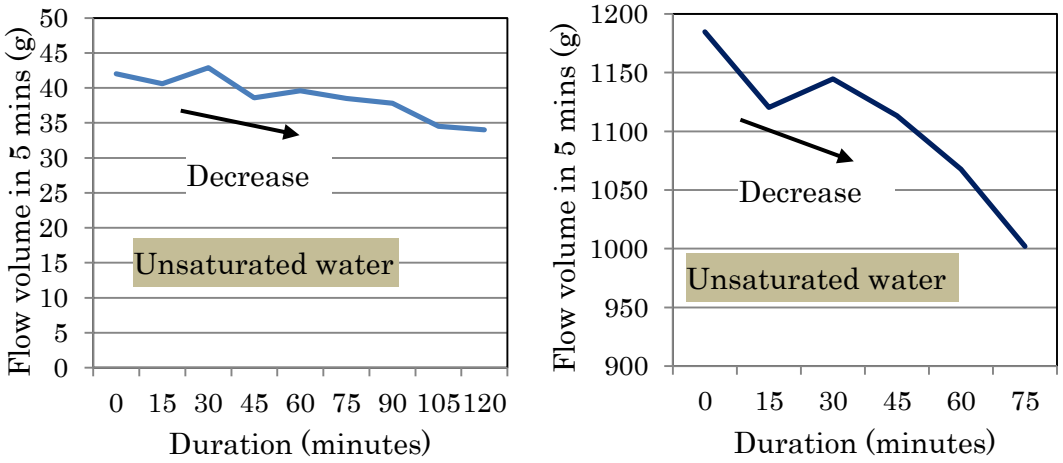

Figure 6-1: Water flow – duration graphs for two specimens, with different flow speeds, and using unsaturated water (less than 100% dissolved air saturation).

Figure 6-1 shows graphs of water flow measurements for two specimens, and with different water flow speeds. Both specimens show reducing water flows with time, and yet no visible air bubbles seem to be growing in the narrow gaps.

In this research measurements were done for 2 hours, at 15 minutes intervals. 0, 15, 30, 45 up to 120. Outflow water is collected starting at the 16th minute for 5 minutes. The collected volume is then weighed, and mass flow rate computed.

In chapter 5, air bubble growth observations were done, and it's clear that air bubbles start growing from very minute sizes and turn into large millimeter diameter bubbles. Observations with the naked eye cannot capture such microscopic sizes; but this does not mean micro and nano air bubbles don't exist.

Ushikubo *et al*, [2] confirmed experimentally and with good precision the existence of nano bubbles in water. By measuring particle size distribution, and zeta potential, and proton spin-lattice relaxation times, they confirmed the existence of bubbles with a few hundred nanometers diameters. Borkent *et al* [3] studied the stability of surface adsorbed nanobubbles, classifying them as 'super-stable' even outside ambient conditions. Through using atomic force microscopy observations on surface bubbles exposed to extreme conditions of negative pressures, the retention of these fine air bubbles could still be observed (see Figure 6-6).

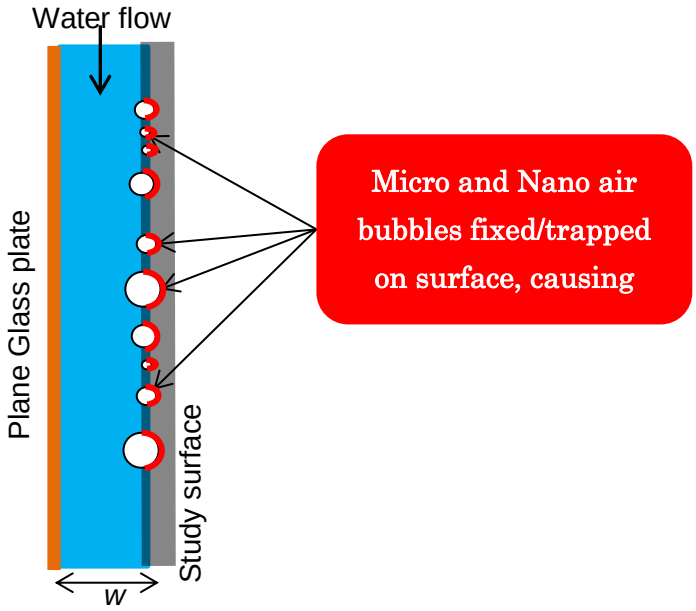

Figure 6-2.: A schematic representation of micro and nano air bubbles fixed/anchored on the surface of water flow, causing water flow braking.

In the same line of thought, it was now understood that: micro and nano air bubbles

fixed or anchored on the surface micro-pore structure of a water flow surface, cause water flow braking in the system. Figure 6-2 illustrates the meaning of this hypothesis. In order to verify the effect of fixed micro and nano air bubbles, additional experimentation was done. Two polished wood specimens of different dent densities, one with density three times the other are used for this further verification.

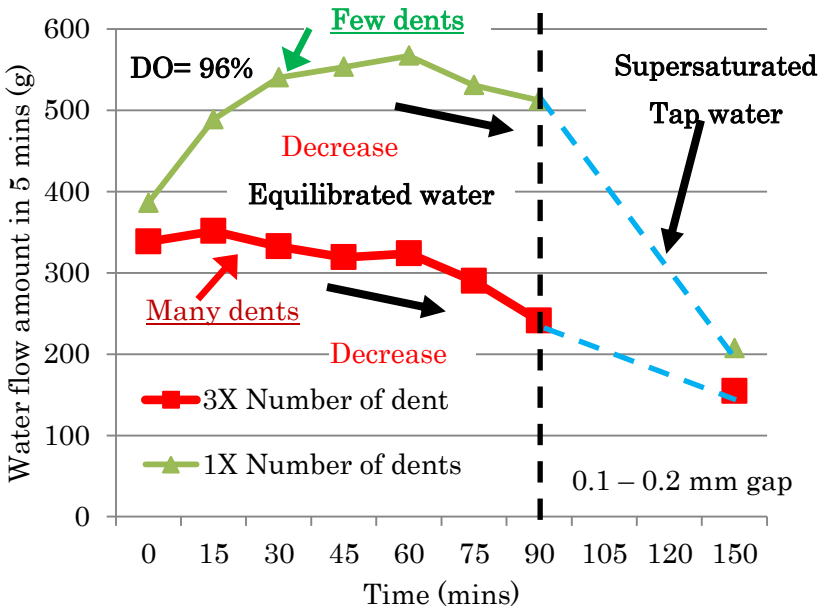

Figure 6-3.: Graph of water flow reduction using equilibrated water condition for two specimens of different dent density.

Figure 6.3 shows the water flow curves for the two specimens (1X and 3X). As previously observed, water flow reduction occurs with equilibrated water type. Still, specimens with higher density of dents reveal faster water flow reduction due to possibly the faster evolution of micro and nano air bubles. In the result of water flow for the specimen with fewer dents, there is an initial increase in water flow amount, and this could be attributed to the usual water flow tendency at the start of water flow tests before stable flow conditions are attained. Or it could be associated with the lower rate of water flow reduction due to fewer number of micro and nano air bubbles. It is however quickly observed that water flow soon follows the expected trend. Or it could an error in measurement of water flow or speciment characteristics.

However, there was still no observable air bubbles, and yet water flow reduction could be measured. In order to investigate further, assisted observation technique was adopted. Microscopic observation of the surface of water flow were done to check for any

evidence of fixed micro and nano air bubbles. Figure 6.4 shows images of no naked eye observable air bubbles, where as Figure 6.5 (where a microscope is used) reveals the several micro and nano sized air bubbles that are fixed on the surface of water within the narrow gap.

To confirm further the air bubble generation ability of these specimens, they were then exposed to supersaturated continuous flow tap water. Within an hour, large air bubbles could be observed to cover more than 50% of the water flow surface. Even in this additional verification experiment, the effect of different dent densities on air bubble growth rate could be noted. Higher dent density specimen showed faster and larger number of air bubbles overall.

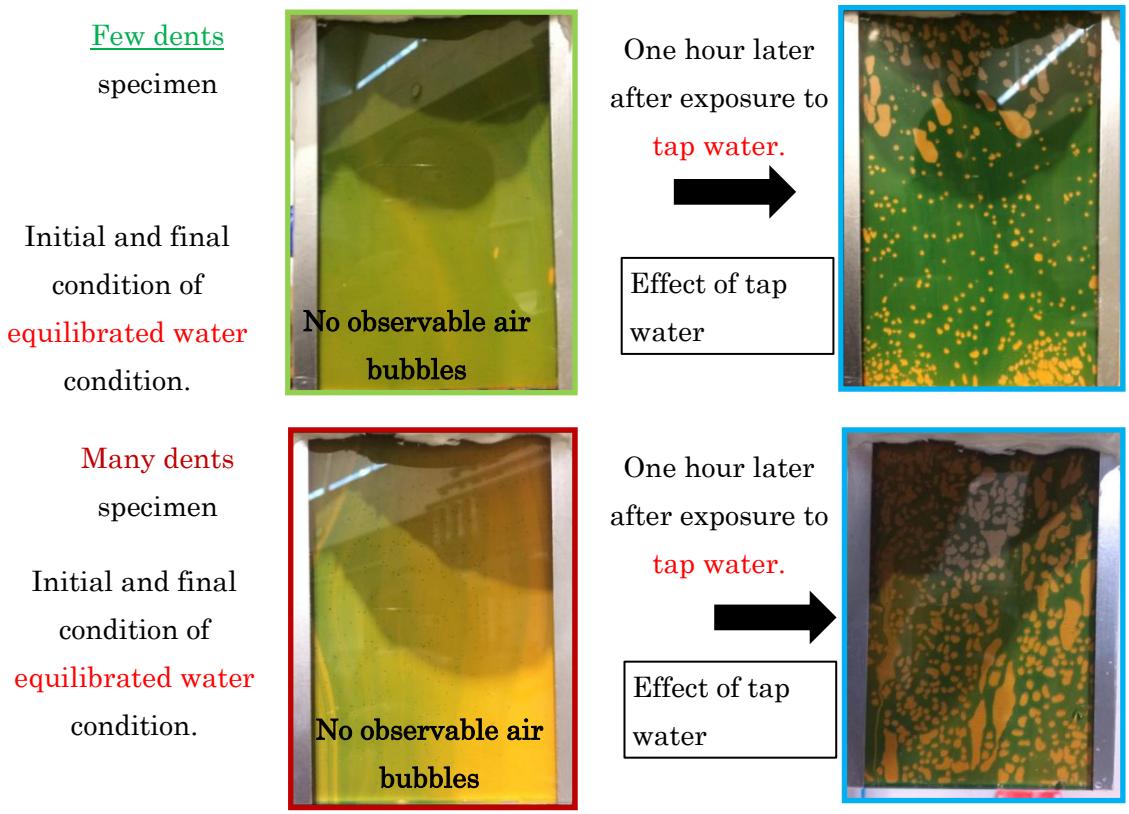

Figure 6-4.: Absence of visible air bubbles while using equilibrated water (left), and effect of using tap water thereafter with quick formation of large air bubbles.

It should however be noted that at the level of microscopic observation and investigations, the relative number and size of fixed micro and nano air bubbles could not be compared for the two specimens.

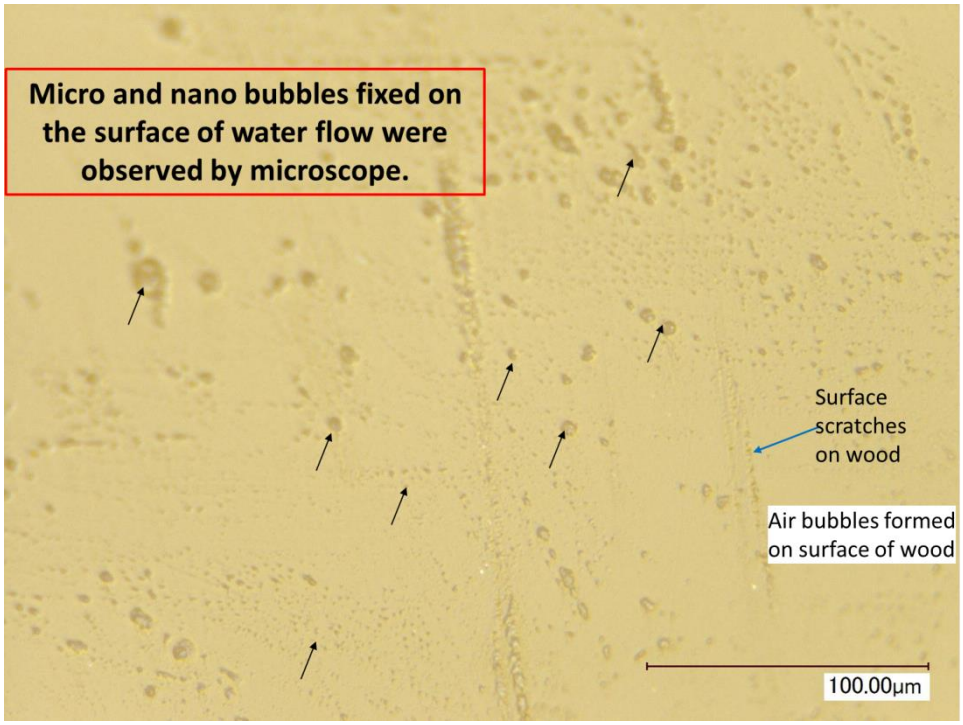

Figure 6-5.: Microscopic view on the surface of water flow for polished wood surface showing fixed micro and nano air bubbles.

At the smaller scales, the surface over which water flows in the narrow gaps is 'rough', full of favorable locations for small air bubble anchorage/fixation. Once formed there, air bubbles start transforming the general outlook of the flow surface. The liquid – solid boundary starts to diminish, as it is continuously being replaced by an air – liquid interface. The drag at the solid wall is now replaced by a 'stronger drag' - the air – water interface. It should be noted that, the air water interfacial size is time dependent, and its creation and growth depend on several other conditions. We have observed air bubble growth with time, and this is indicative of the growing effect of the air bubble.

Li *et al*, [4] discusses the characteristics and persistence of fine air bubbles in water, and how it can be applied in groundwater bioremediation. Air bubbles exist in water for long periods of time because of their high electrical charge density that prevents them from coalescence, and this also contributes to their stability in water.

Figure 6-1: shows water flow tests measured at 15 minutes intervals, using equilibrated water. Equilibrated water (water at just below 100% air saturation) is usually not capable of growing large size air bubbles in the narrow gaps. However, micro and nano air bubbles can still be formed, and contribute largely to water flow braking. The

difference with using supersaturated tap water is that, supersaturated tap water forms and grows these nano and micro air bubbles quicker. Therefore, water flow reduction occurs faster with supersaturated water than with equilibrated water. Though not investigated, it is anticipated that equilibrated water can only grow air bubbles only up to a certain size; beyond this, supersaturated water would be necessary.

The water flow braking mechanism of fixed micro and nano air bubbles reveals a lot concerning the nature of the air – water interface. See Chapter 7.

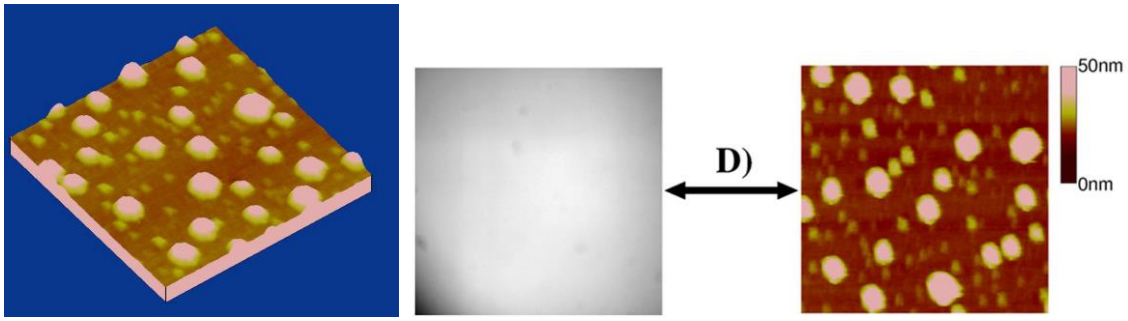

Figure 6-6: AFM topography images of surface nano bubbles stably present, long after cavitation experiments. (Borkent et al, 2007)

In recent years, and with the improvement in imaging techniques, the nature of water, and interaction of water with air is becoming clearer. Recent observations with atomic force microscopy have recently revealed more about the puzzling natural of nano and micro air bubbles [5], [6], [7], and [8]

6.2 Limitations of traditional water flow equations

The traditional water flow equations of Hagen Poiseuille, Darcy and Washburn have included in them material factors to cater for the varied nature of flow paths. However, over time, the surface properties change and the initially assumed factors become obsolete. In the modified Hagen Poiseuille equation for example (Eq. 1), for self-healing water pass testing, the material factor is based on the rough surface nature of concrete. It assumes a liquid – solid interaction [9]. Based on our observations and water flow measurements, the surface make-up gets changed to an air – water interface for example (see Figure 6-2). And this is a gradual process, depending on the existing conditions. Surface factors have been cited to affect flow parameters in several experimental measurements [10]

All these findings point to the limitations of these formulas in predicting water flow

amounts through parallel plates, channels and porous media. There is probably need to further modify or provide appropriate material factors.

6.2.1 New understanding of water flow reduction

Water flow reduction occurs due to the following causes

1) Braking mechanism of nano and micro air bubbles

2) Blocking mechanism of large air bubbles

3) Narrowing of flow paths due to actual self-healing mechanisms

Figure 6-7 shows the evolution of, and understanding of water flow reduction in narrow interfaces. It gives a macro to micro perspective, and as micro fluidic systems and nano technology applications become widely developed, this microscopic understanding is necessary.

In self-healing techniques, water flow reduction in cracks or narrow gaps should occur by actual deposition of healing products; the air bubble growth and thus braking and blocking mechanism is a coincidental occurrence and is usually not the original intended purpose of self-healing materials.

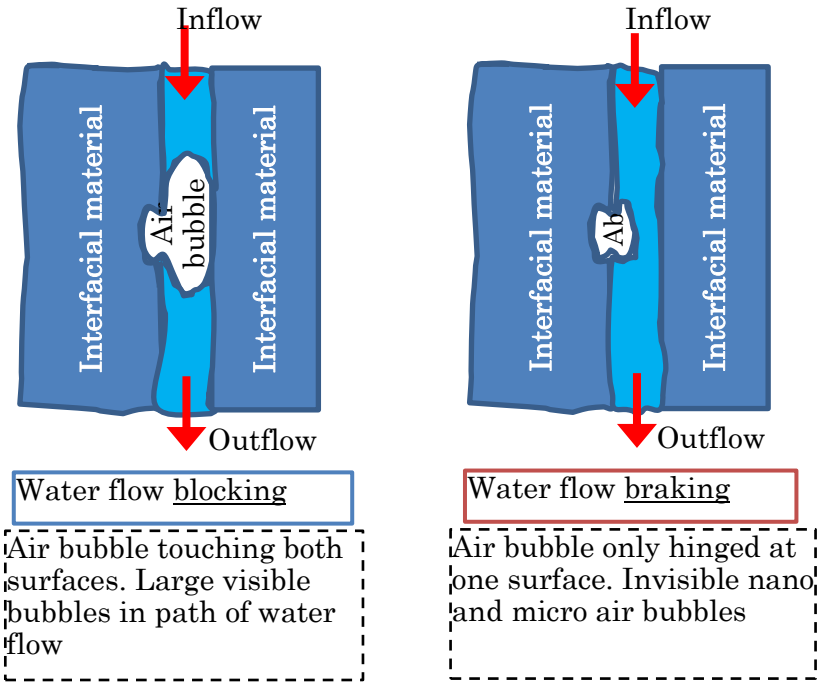

Figure 6-7: Illustration of the two predominant mechanism of water flow reduction due to fixed air bubbles in narrow gaps.

6.2.2 Micro and nano air bubble effect in narrow gaps

The new understanding of water flow reduction stems from the strongly notable water flow braking effect of micro and nano air bubbles fixed or anchored on the micro-pore structure of concrete and other study materials. Besides the water flow reduction, in micro systems containing water, or experiments, several effects have been attributed to the existence of these fine air bubbles in the systems [11], [12], [13].

In microfluidic systems and devices, efficiency has been observed to be affected by the presence of air bubbles [14]. Heat conduction for example, or temperature drops in such small systems can vary due to existence of such air bubble nuisance, as seen in Figure 6-8 by Schneider *et al.* In most of the highlighted cases of air bubbles affecting systems, the air bubbles are not necessarily fixed on the flow surface, as envisaged in this research. For such cases, multiphase (air and gas) flow is sufficient to cause significant changes in measured parameters.

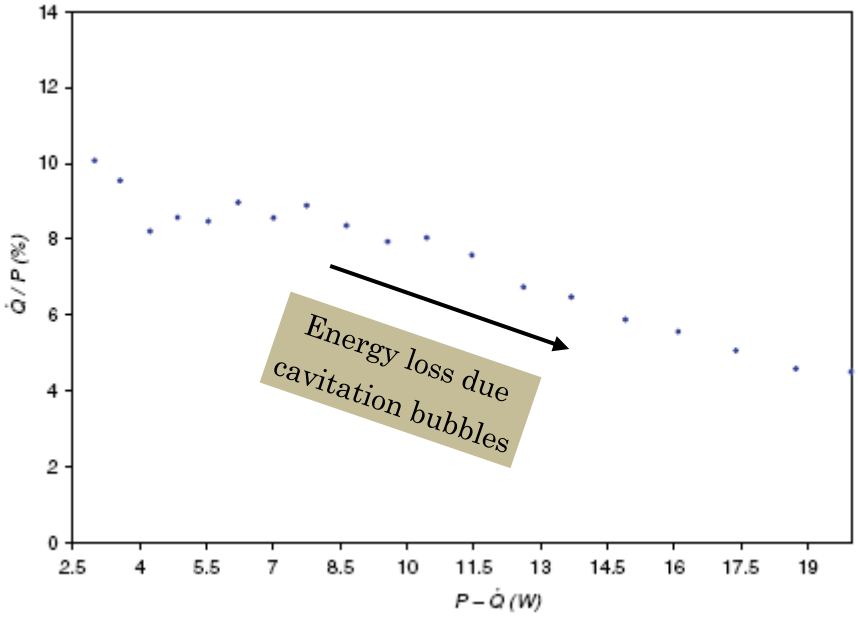

Figure 6-8: Heat loss curve for cavitating flow conditions for refrigerant through micro channels, of about 5-10% heat losses, (Schneider et al, 2007)

6.3 The air bubble anchorage hypothesis and mechanism of water flow braking

How do micro and nano air bubbles cause water flow braking? The mechanism of water flow braking by nano and micro air bubbles points to the nature of the air – water interface. The hypothesis is that, water molecules at the air – water interface are

strongly fixed in position, whereas molecules of water just away from the interface are freely moving about in the bulk. Water molecules at the interface have restricted rotational movement compared to those in the bulk water. So, within a few molecular layer(s), water exists as a 'solid' phase! And just away from it, in the subsequent water layers and in the total bulk, water exists as a liquid. The strong hydrogen bonds still exist, but this time, they are bonding to a fixed water layer. As water molecules flow past the fixed layer, they are slowed down by both the attraction of polar parts of the fixed interfacial water molecules. This mechanism becomes bigger with interfacial surface area and as more and more air bubbles form new surfaces.

It is also important to note that in some research the presence of nanobubbles on hydrophobic surfaces submerged in water may lead to an invalidation of the non-slip boundary conditions [15]. This would then directly have an effect on fluid flow where such bubbles exist on hydrophobic surfaces.

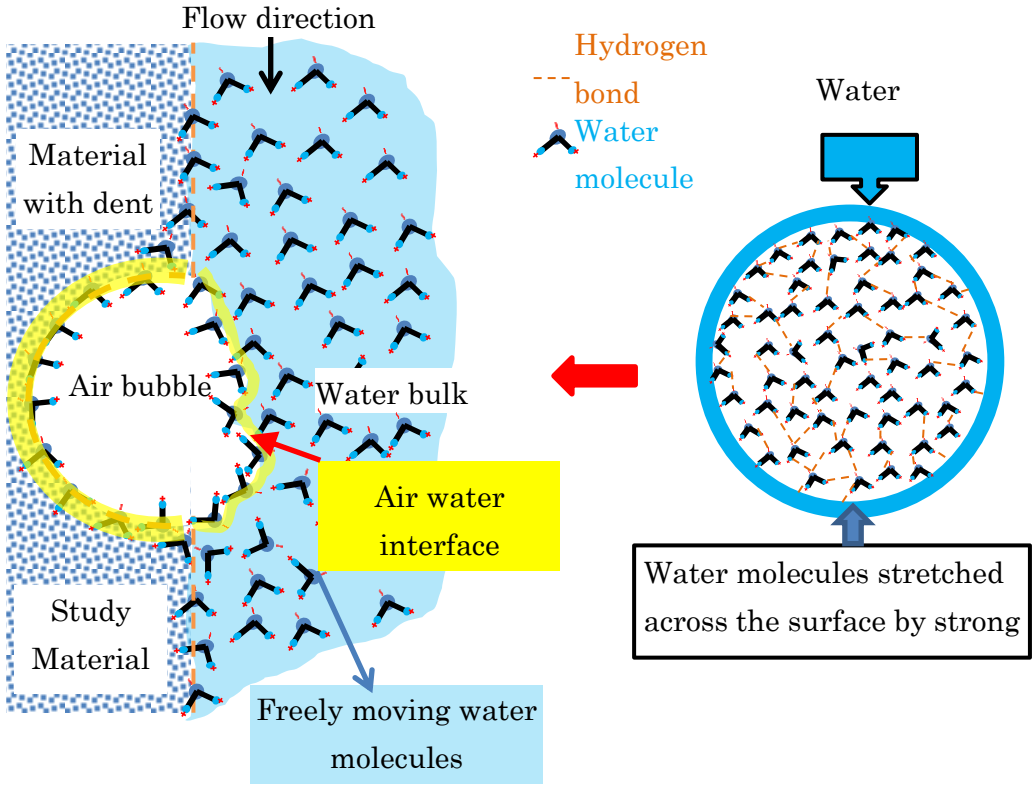

Figure 6-9: A schematic depicting the fixed nature of the interfacial water molecules at the air – water interface. Water flow braking is caused by the fixed nature of these water molecules, plus their limited rotational ability.

Figure 6-9 shows a schematic of the fixed air – water interfacial molecular hypothesis. Based on current measurements, and the strange nature of water molecules, plus the numerous literatures that points to the peculiarity of surface water molecules, the hypothesis is based. Chapter 7 attempts to provide evidence that backs up this hypothesis from an experimental point of view.

6.4 Chapter summary

Chapter five reveals the new understanding of water flow reduction due to braking mechanisms of surface fixed nano and micro air bubbles. It also clarifies on the previous understanding of water flow reduction due to the blocking mechanism of fully grown air bubbles in narrow gaps of water flow.

In this chapter, plenty of research supporting the existence and stability of nano and micro bubbles has been reviewed. It's true that the sheer existence and stability of nano bubbles still baffles many researchers, but with advances in imaging technology such as AFM, the evidence of their presence and stability is increasingly becoming common. This falls in place to support our inferred understanding that in their small size, micro and nano air bubbles that are fixed on the surface of water flow can cause notable water flow braking – especially for smaller scale water permeation.

Additionally, it is important to note that these finer air bubbles are capable of affecting other functions of systems, such as heat transfer or even cause pressure drops in hydraulic set-ups where they happen to manifest.

For this research in particular, direct observation of these said finer air bubbles needs to be proved in order to support the fundamentals of their contribution to water flow reduction.

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Chapter 7 The air – water interface and surface tension theory

The air water interface comprises the biggest part of this study in understanding the mechanisms of water flow reduction in narrow gaps. In order to clearly emphasise its effect, the microscopic meaning of surface tension is brought into focus. Although not clearly understood, the air – water interface plays a fundamental part in the functioning of nano and micro water systems and devices. Our new understanding of water flow reduction in flows through narrow gaps points to the strong effect of the creation of a new interface, the air – water interface. Water molecular behaviour at the air – water interface, and how it varies from the bulk counterpart is explained in this chapter.

7.1 Air exchange concept at the air – water interface

Air bubble growth happens due to either air expansion inside the bubble, or due to new air molecules entering the bubble causing an increase in pressure [1], [2], [3]. In this research, the latter is hypothesized. Air bubbles grow or disappear by air exchange across the air – water interface (see Figure 7-1). There is a mechanism by which the partial pressure of air in the bubble is increased to equate to that in the flowing water, and in the process leading to gaseous entry from the water and into the air bubble, and vice versa.

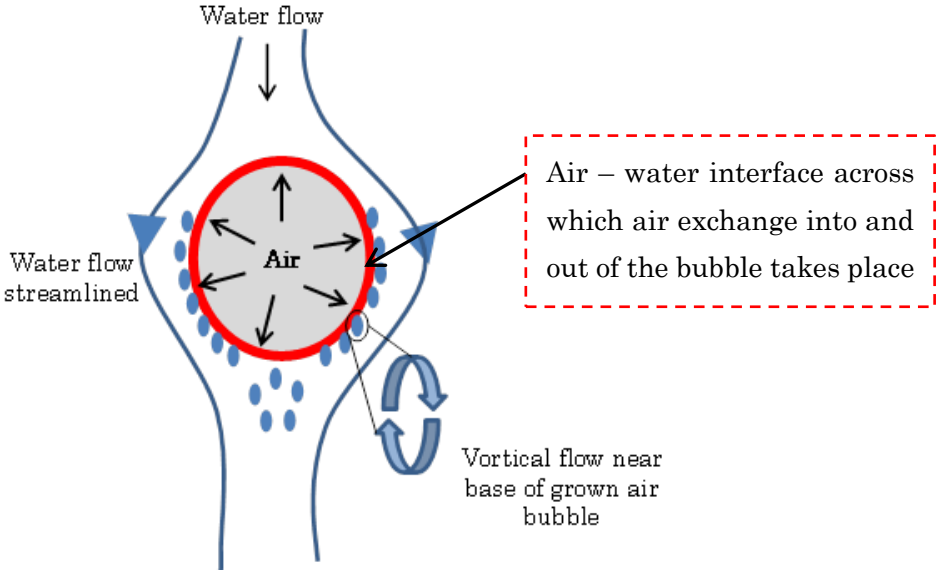


Figure 7-1: The air – water interface (red circle) depicts a transitional thin boundary between the two phases, air and water.

In supersaturated bulk water condition which is left to stand, air bubbles are created by the same mechanism. The water surface continuously allows dissolved air to join the bulk atmospheric air, while at the same time, small bubbles may form at several points on the inside surface of the container. Until partial pressures of dissolved gasses are equal, air exchange continues to take place.

In supersaturated water conditions, the air bubbles have a tendency to grow [3]. This is because the restricting surface tension forces are counteracted by excess gas diffusion into the air bubble, until equilibrium is attained. Air bubble growth observed in this research takes place under supersaturated tap water conditions. Thus, air exchange is largely from the water into the bubble, except in reverse air bubble growth, in which case the supply air deficient water destabilizes the system and with the surface tension force, air is quickly taken out of the bubble and back into the water. The process is however gradual and is largely time dependent in both directions.

7.2 The air – water surface and the concept of surface relaxation

The surface of water possesses properties that change from time to time [4]. For example dynamic surface tension of water, the diffusion of surfactant contaminants from the aqueous phase to the surface, reorientation of surface water molecules' dipole moments, etc. [5]. Surface relaxation reveals that surface tension at the air – water interface lies between 80 – 100 mN/m, depending on temperature, and that it relaxes to equilibrium value in about 1 ms. This is attributed to a restructuring process taking place in the first few milliseconds after creation of the surface. These processes determine the surface charge on the water surface, orientation of water dipoles at the interface, and other surface properties [6], [7].

The negative surface charge at the interface in some literature is mentioned to be due to a preferred orientation of water at the interface, of forming dangling O – H bonds away from the bulk as shown in Figure 7-2. A surface relaxation refers to the re-orientation time of dipoles when a new surface is created [8], [9], [10].

Figure 7-2 shows an illustration of the dangling O – H bond at the air – water surface. It depicts that water molecules at the surface have the O-H bond pointed out and vibrating about in the air. The figure also reveals the decrease in water density towards the air – water interface. This revelation in this research [8] is contrary to what was previously believed about the abundance of water molecules at the interface.

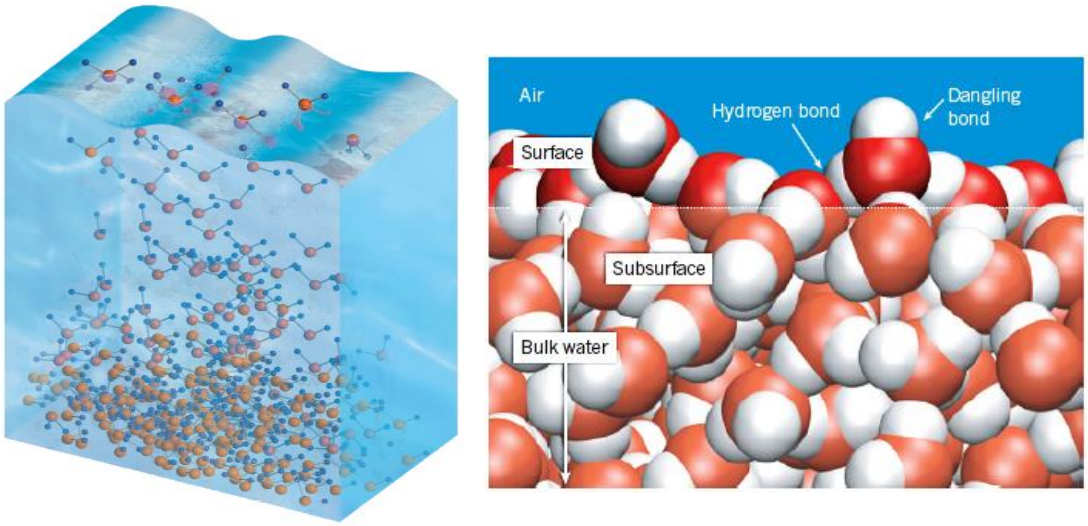


Figure 7-2: A depiction of the air – water interface, with hydrogen atoms oriented out in the air and the dangling O – H bond. (Mundy et al, 2005; Stiopkin et al, 2011)

7.3 Popular theory of surface tension of water

Liquid water surface behaves like a stretched surface that's under tension. This stretch, equal in all directions across the surface, gives the water surface, properties completely different from the bulk [11], [12]. In the basic understanding, there is force acting on the surface water, just like at all liquid surfaces. Traditional understanding of the surface tension theory relates it to the forces of attraction and repulsion between molecules. That, while molecules inside the water exist at an equilibrium distance of no net repulsion or attraction, those at the surface are further apart, and thus attract each other (cohesiveness) [4], [13]. This attractive force between surface molecules is what keeps them from being pulled into the liquid bulk as illustrated in Figure 7-3. This energy imbalance at the surface is the basic or textbook understanding of surface tension. Figure 7-3 shows an illustration of this popular theory of surface tension [14].

Surface tension of water means that there is a layer of water molecules at the surface that is dynamically not in balance with molecules within the bulk liquid. In dealing with bulk water systems and phenomena, this basic understanding is adequate and can be used to explain water surface behavior in a relatively simplified manner. This is because, the size of this pristine water molecular layer is totally negligible compared to the overall behavior of the entire liquid. However, once we narrow down the size of the bulk part, to within a few orders of magnitude of the size of this pristine layer, the behaviour becomes different and may no longer be explained in a simplified way.

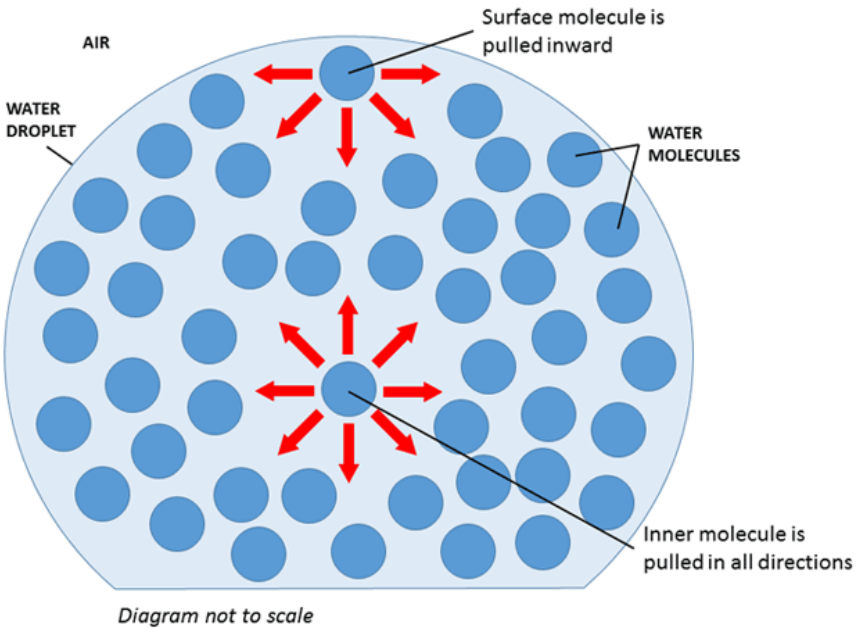


Figure 7-3: Diagram of surface tension forces acting on water molecules in a liquid droplet. (Funio et al, 2015)

7.4 Microscopic theory of surface tension

As researchers start investigating smaller and smaller dimensions of materials, they face similarly varied material behaviour. Properties of single molecules for example are totally different from those of an aggregate of the same molecules. The effect surface tension is not so important when dealing with water flow in large pipes. But once we start studying micro-fluidic flows, water surface tension becomes relevant. This requirement, coupled with other phenomena and observations can no longer be simply explained in energy terms. Yang *et al* attempts to elucidate a molecular theory of surface tension for a one component system, by determining the density profile in the interfacial region [15].

In trying to understand this research of water flow in narrow gaps, plus the observed creation and presence of nano and micro air bubbles, an energy viewpoint of surface tension is not enough to explain the observations [16]. Similarly is the behaviour observed by other researchers trying to study water at finer levels [17], [18], [19], and [20], [21]. A deeper investigation of these various research findings still reveals colliding understanding in trying to uncover the mystery of water's surface. For example, on the arrangement of water molecules at the surface, or the strength of hydrogen bonds, or the charge at the surface of water! However, what they all agree on is the mysterious

nature of the surface of water, a clear understanding of which is necessary to propel scientific exploration a step further.

7.4.1 Adhesive and cohesive property of water

In the bulk, water molecules are held together by forces of attraction, and this gives them their cohesiveness. The water molecule is polar due to the stronger attraction of hydrogen electron by the oxygen atom in their covalent bonding style. There is thus a resultant partial positive and negative charge on the hydrogen and oxygen atoms respectively (see Figure 7-4). This is the origin of the famous hydrogen bonds in water, the intermolecular attraction between the partial opposite charges on the water molecules. This behaviour is the basis of water's outstanding properties such as being a universal solvent. Within this unique behavior lie a lot of unchartered territories concerning the behavior or water.

The adhesive property of water too originates from water's polar structure. Water molecules are attracted to other material molecules. The adhesiveness of water doesn't break its cohesiveness, and this is the origin of capillarity! As water rises in a glass tube, there is continuous adhesion with the glass, and cohesion within the water molecules. In fluid flow, the no slip boundary condition is usually assumed, and it implies that at the interface between liquid and solid, velocity is zero. This is because of the drag force which is related to viscous friction. In general, all these surface flow phenomena are related to water's cohesive and adhesive properties, plus the hydrophilic or hydrophobic tendencies of surfaces [4].

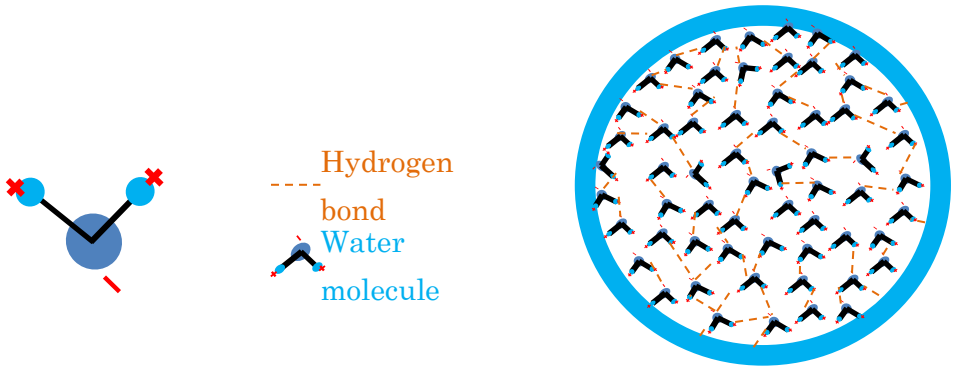


Figure 7-4: Schematic of the polar nature of the water molecule and how it leads to hydrogen bonds in bulk or surface water, and also determines hydrophobic or hydrophilic interactions with other substances.

7.4.2 Newtonian and non-Newtonian behaviour of water

In a general sense, water is considered to be an ideal Newtonian fluid. However, its

non-Newtonian behaviour becomes evident at small scale considerations. The unique behaviour of water is in this research linked to the non-Newtonian behaviour. Water too, is considered an extreme case of Bingham fluid, at least requiring a certain minimum yield stress before it starts behaving as a Newtonian fluid. For water flow through nano and micro slits, water flow behaviour is observed to be different from Newtonian flow, although it is not yet so clear why and what causes this behaviour [22], [23].

In Figure 7-5, it is implied from the unique behaviour of water in fine spaces that water probably behaves as a Bingham fluid, with a yield stress in very narrow gaps, and that this characteristic could determine several of the observations in such spaces.

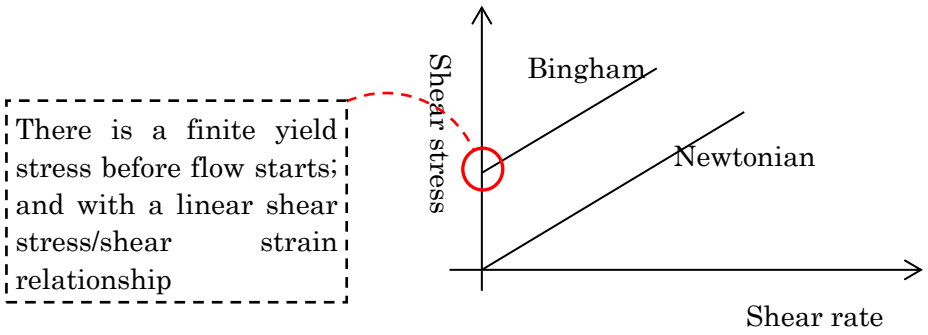


Figure 7-5: Graph showing the classification and differentiation of Newtonian and Bingham fluids.

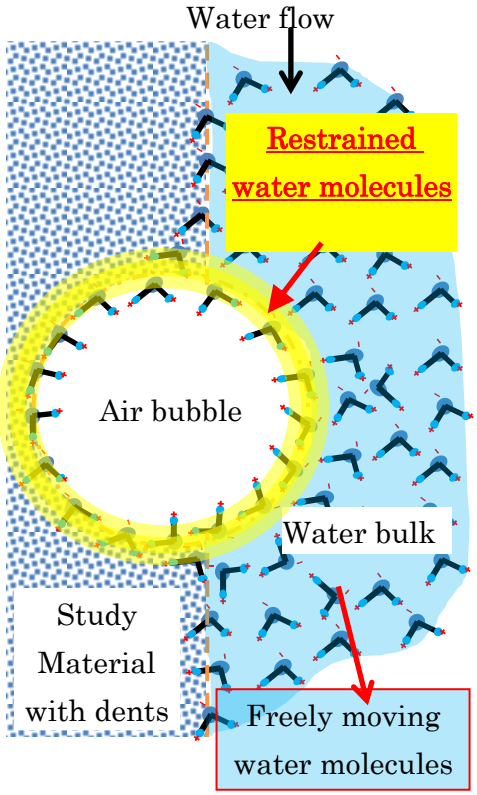
7.4.3 Proposed theory on the nature of the air – water interface

The air – water interface is a fundamental part of this research work. Its nature is what is hypothesized to be the cause of the drastic water flow reduction that is observed for permeating flow through narrow interfaces, plus the air bubble growth mechanisms. Based on the several experimental observations and theoretical understanding of the nature of water, a theory on the nature of the air – water interface has been proposed.

7.4.4 The fixed water molecular structure hypothesis/thin water layer.

The proposed hypothesis points to a structure of interconnected water molecules at the air water interface. Figure7-6 shows an illustration to reveal the strong interconnection, and restricted rotation by water molecules in this thin water layer. In the traditional surface tension theory, surface molecules are known to be pulled into the bulk of water, but it's not clear concerning the orientation, or rotation, or their fixed nature. By this proposed hypothesis, we attempt to put forward a new understanding of the possibly restricted rotational ability of outermost surface water molecules. What this means is that, if this fixed interface is attached to or anchored to an immobile surface, then it will

stay in place. This is one of the reasons why air bubbles created in narrow interfaces cannot be washed out by flowing water, as per the observations of this research. The surface tension force is quite strong in keeping the air pocket together that it cannot easily be broken. If this air pocket is trapped at a crevice, surface tension would act to compress it, but then, if equilibrium is attained, the bubble stays intact as long as water is present around it.



Water molecules at an air – water interface assume a fixed water molecular structure with minimal molecular rotation compared to their bulk counterparts. It proposes that the water surface is made up of a fixed water molecular structure, of a few water molecules thick towards the bulk water.

Figure 7-6: An illustration of the varied nature of interfacial molecules compared to the bulk ones, at an air – water interface.

7.5 Experiments to support the fixed interfacial water molecular structure

Experiments in chapters 3 – 6 reveal that there is more to the observations than we can literally see. These observations are however a result of the nature of the air – water interfaces. In the following experimental investigations, attempt has been made to reveal the validity of the above hypothesis. Experiments have been designed based on the hypothesis of a fixed water molecular structure at the interface. Discussions based on daily observations of water behaviour have also been presented.

7.5.1 Air bubbles at the surface of water

It is interesting to watch air bubbles that are naturally formed at the water surface without any catalysts such as foaming agents. The behaviour of these bubbles, though short-lived is usually revealing of the nature of the interface. A bubble at the surface of water that's exposed to the atmosphere does not sit tangential to the water surface, but rather maintains a spherical shape. Figure7-7 shows air bubbles formed on water surface and later frozen to study the shape of the bubble at the surface of water.

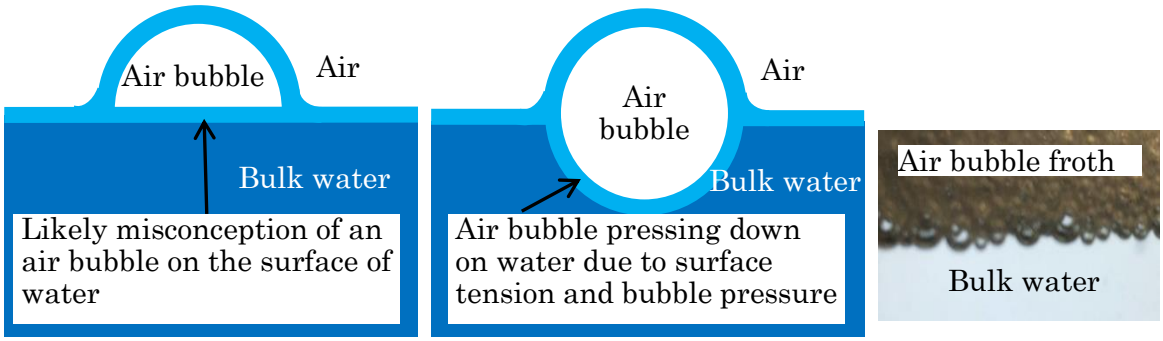


Figure 7-7: Air bubbles at the surface of water reveal more of the nature of the air – water interface. Maintaining the spherical shape is the work of both surface tension and the nature of water molecules at the interface.

An air bubble cannot rotate at the interface! If the water around it is moved, it moves as a whole. This means that the water molecules that hinge the interface cannot be rotated to enable allow air bubble to spin at the meniscus. If it is to rotate, a necessary minimum force must prevail.

7.5.2 The spinning floater ball effect

This experiment was designed based on buoyancy, water flow, and the fixed nature of the air – water interface. A floating ball of diameter ranging from 3 – 5 mm is placed in a dent (depression) on a given study surface. The dent is semi spherical with a diameter larger than the ball. The ball freely moves about in the depression created. With this set-up, a glass plane is placed, leaving a clearance less than the diameter of the floatable ball. Even in this state, the ball can freely be moved about by the motion of the specimen set-up. The set-up is now ready for investigations. Once the set-up is saturated with water, two possibilities can be observed.

The dents represent the several pores that line most surfaces, and are nucleation points for air bubble creation and anchorage. Therefore, it is expected that, depending on the suitability of the dent, an air – water interface will be created. If it extends and touches

the ball, the floating ball will not be able to spin. In a dent without any formed and fixed air bubble, the ball will continue spinning in a given direction.

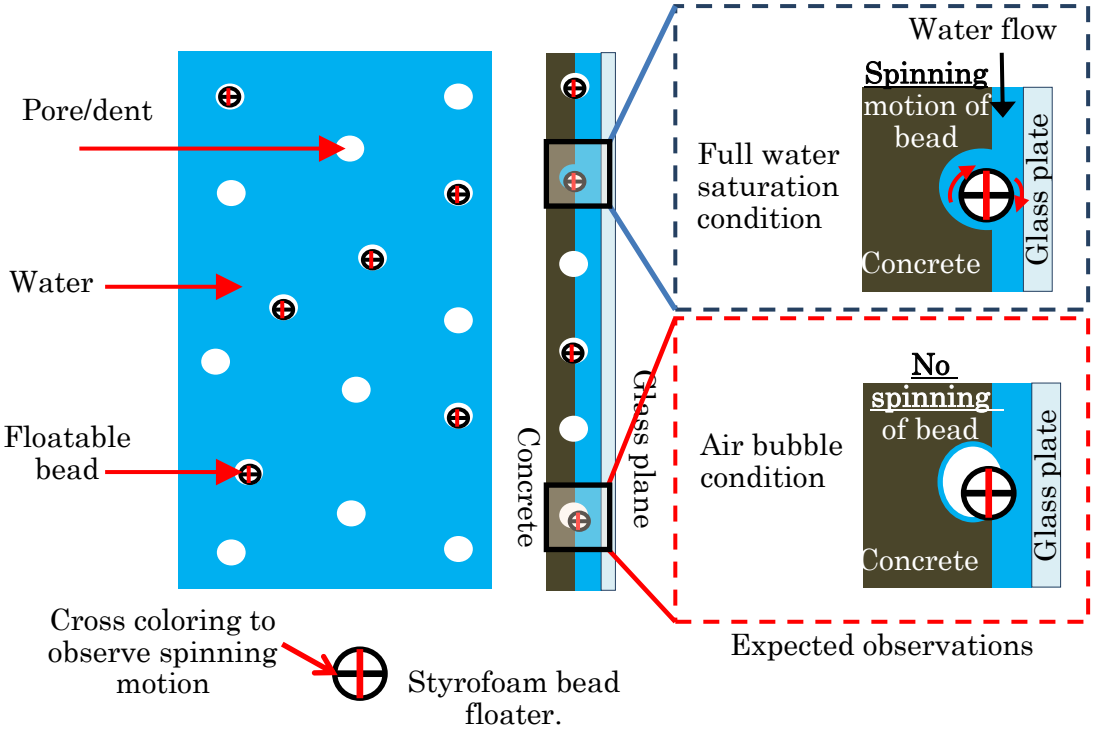


Figure 7-8: An illustration of the experimental set-up of the spinning ball effect to study the anchoring effect of the air – water interface.

In this experimental set-up as illustrated in Figure 7-8, it was observed that the ball in a dent where a fixed bubble is present and there is an intersection between the two, spinning of the ball was dampened to zero. In a dent where no air bubble is created, and the ball is completely submerged in water, spinning continues as long as water flow takes place.

This test was based on the principle or buoyancy and spherical rotation (see Figure 7-9). Buoyancy causes the ball to rise up out of the gap, and the flowing water acts to prevent the ball from coming out of the dent. As a result, a moment acts on the ball causing it to rotate continuously as long as water is flowing between the two surfaces.

The critical part of this experimental design is to reveal the anchoring effect of an air bubble depicted by the inability of the ball to spin in the presence of an air interface. This serves to reinforce the hypothesis that the air water interface is composed of a fixed water molecular structure, and if this fixed layer interfaces with the spinning ball, the ball spin is either dampened or completely stopped.

Through video recording this observation was continuously made for a well-designed set-up. There is a necessary flowrate to cause the ball to spin. Too fast and the water pushes it to the base of the dent, or too slow and the ball floats to the top part of the dent. These considerations have to be made to achieve optimal spin parameters (flow speed, ball size, and vertical orientation of set-up).

In order to clearly understand the mechanisms involved in this experimental set-up, surface adsorbing molecular solution was used. Surfactants tend to adsorb at the air water interface, and would thus change the nature of the air – water interface. A common soap solution was used to cause soap molecules to adsorb at the initially created air – water interface.

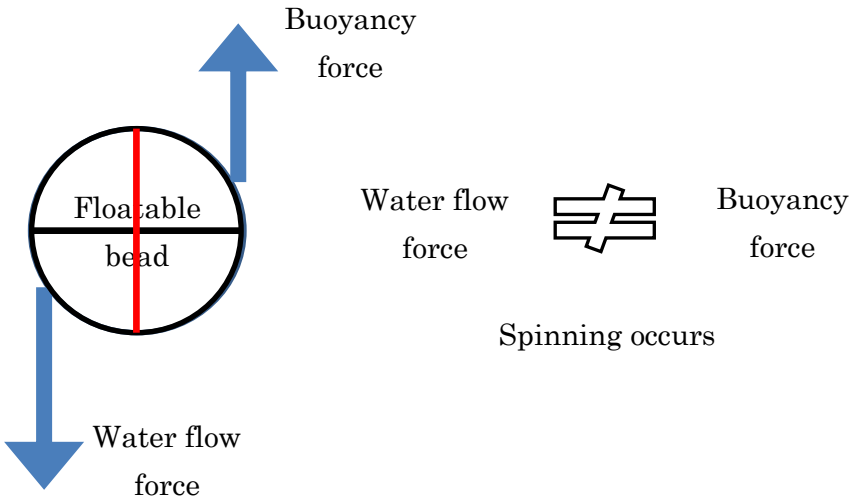


Figure 7-9: Spinning of the ball occurs when there is a resultant couple acting on the floatable bead to cause rotation.

With the same set-up, especially for the no-spin condition of the ball, soap solution is added to the supply water. Addition of soap solution to the set-up immediately causes the ball to spin. This is because, once the surfactant molecules are supplied, they immediately adsorb at the air – water interface, replacing the fixed water molecules. Once this happens, rotational ability at the interface is enabled, and the spinning of floatable ball is started. This is one of the evidences to support the hypothesis that the air – water interface is structurally composed of water molecules with restricted rotational ability, and that it would require a considerable/ minimum effort to break through it. The traditional surface tension theory highlights this from an energy perspective. In this research, a microscopic and molecular perspective of the true nature

of the interface is discussed.

7.5.3 Vibrating water film at the air – water interface

Although this was just an observation made during water flow over an air bubble, it is important to discuss how it relates to the fixed nature of the air – water interface. It is first of all important to note that in this experimental set-up, water is caused to flow over the surface of an air bubble. It is a prerequisite for the stability of the air bubble, and to keep it in place. Water flow over the interface causes it to vibrate. The vibration is due to the tendency of the flowing water's attempt to wash out a fixed thin layer of water interfacing with air. Ripples can be observed at the interface, plus a bottom compression tendency at the lower part of the bubble.

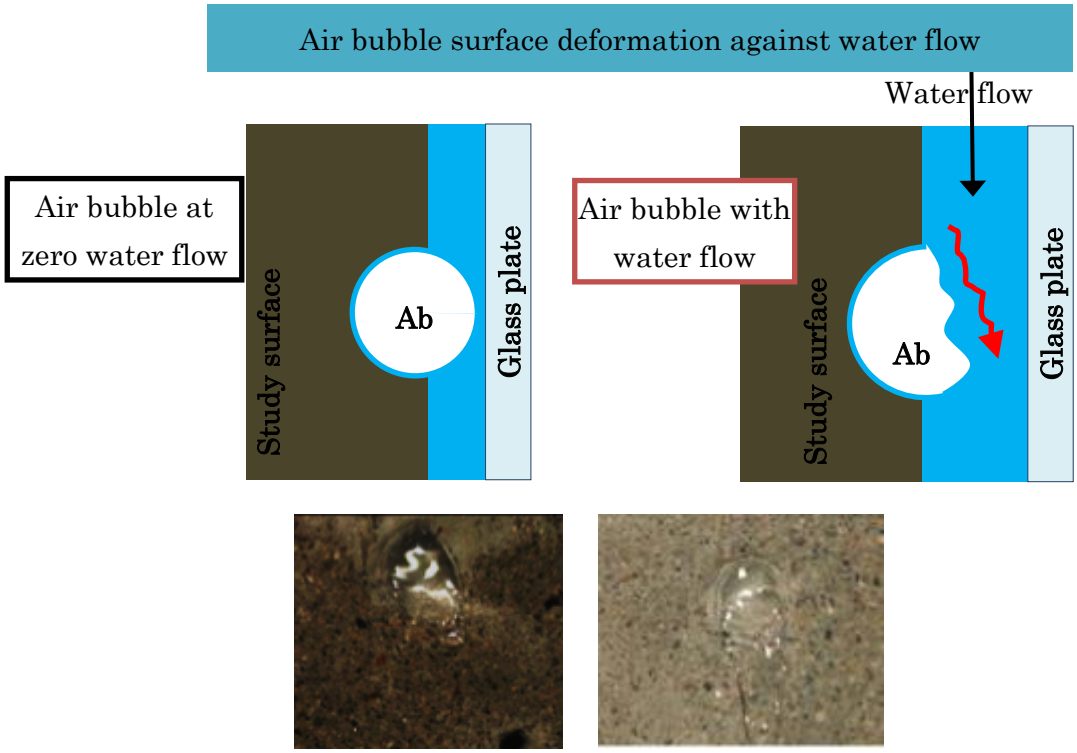


Figure 7-10: Vibration of the air – water interface observed during water flow in a 3mm gap with fixed air bubble.

When a surfactant solution is added to the supply water, the surface smoothens out, and the ripple tendency disappears. This observation could be explained by the same effect of surfactant molecules at the interface. The smoothening of flow is due to increased rotational ability of interfacial molecules (water or surfactant). Figure 7-10 shows the difference between the two surfaces before and after adding surfactant solution to the flow set-up.

7.5.4 Luminescent particle retention at the air – water interface

In reality, it is currently impossible to see water molecules in their individuality. All we know about the interface is deduced indirectly through experimentation and simulations. When we attempt to make observations at the interface too, we can't observe molecules that are fixed, but we can indirectly, through a different approach come to deduce the nature of the air – water interface, as shown in Figure 7-11.

Luminescent substances emit coloured light to reveal their presence under ultraviolet radiation. Water molecules are incapable of this, as far as the author knows. Thus in plane and normal light conditions, the air – water interface will possess the colour of water or that of the material directly behind (in this case the material the dent is formed). In the dark, no luminescence is possible, and minus even with UV light, the plain air – water interface remains meaningless.

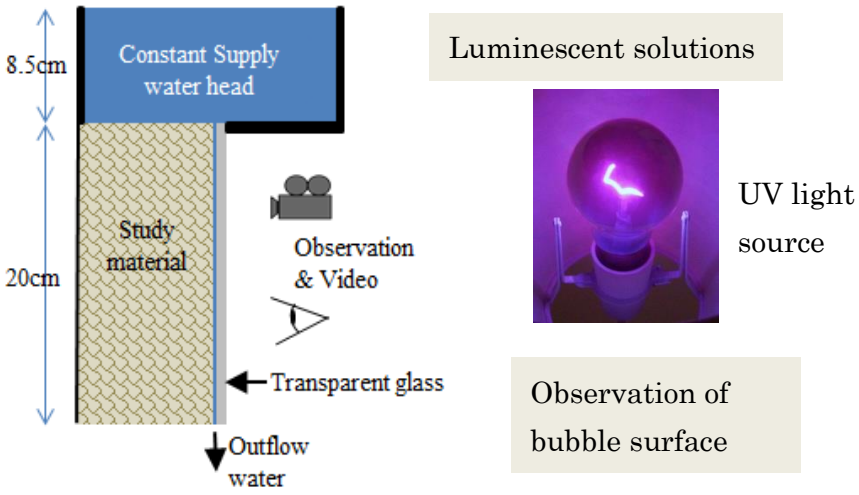


Figure 7-11: Set-up to utilize ultra violet radiation to observe luminescent molecular adsorption at the air – water interface.

In order to study further and reveal the fixed nature of water molecules at the interface, luminescent solution was used, just like the surfactant molecules. It was added to the supply water that interacts with the interface, in a sequence shown in Figure 7-12. When the luminescent solution is added to the set-up, the colour can initially be observed under normal lighting conditions, but is soon washed out. It should be noted that, continuous tap water is maintained during the process. This is what flushes out any colour or loosely held contaminant molecules.

When the luminescent colour seems to be flushed out, the interface appears as was initially. When UV light is turned on, only the air bubble film becomes visible. Its outline, plus the visible surface are coloured by luminescent molecular colours. This again further reveals the nature of the air – water interface. Why is there luminescence at the surface of the air bubble? This explained by either the entanglement or adsorption of luminescent molecules at the air – water interface. This observation can only be made under ultra violet lighting conditions. Under normal lighting conditions, adsorbed molecules at the interface cannot be deduced. Figure 7-13 shows the observations made under normal light and UV light for the same specimen and set-up.

In order to investigate the adsorption strength for the luminescent molecules at the interface, continuous tap water flow is maintained for the set-up. This means that, water is continuously running over the interface. Once added to the set-up, the luminescent colour seems to be flushed out within less than 10 seconds of water flow. In this research, up to one hour observation has been done. The luminescence is maintained for one hour at the interface of air and water. It is expected that it could go on longer, with just decreasing luminescence with time. However, until when it becomes zero has not been determined in this research.

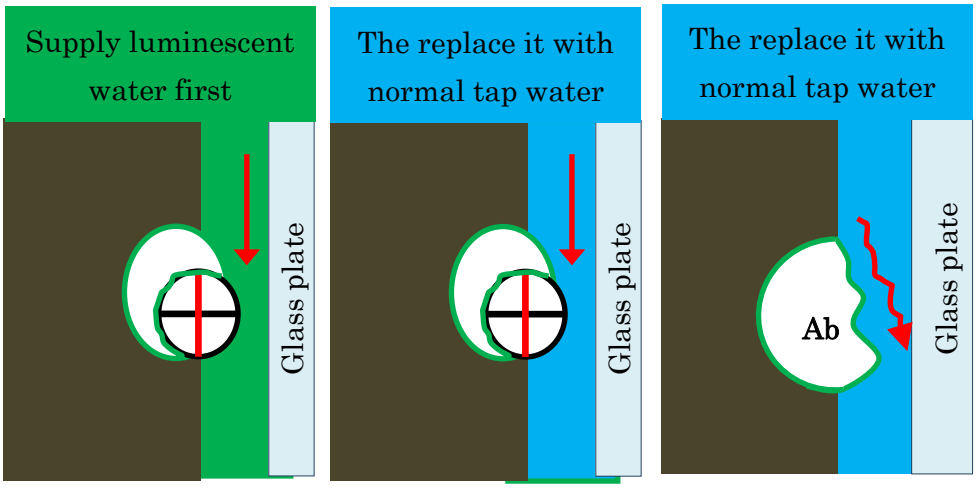


Figure 7-12: A sequence of events while using luminescent molecular solution against tap water flow in the narrow gaps.

This observation (as seen in Figure 7-13) in particular deduces a lot concerning the validity of the hypothesis. The fact that luminescent molecules can only be seen at the air bubble interface means that they are hinged onto something, and we suspect two possibilities

1. Initially the interface is made up of fixed water molecules that behave just like luminescent molecules, i.e., fixed in position. And when luminescent solution is supplied, its molecules get adsorbed at the interface, replacing the fixed water molecules, or

2. When the luminescent solution is supplied, its molecules get entangled in the fixed water molecular structure. Luminescent molecules are of long chains, and it's possible that entanglement could occur. They could be trapped at the interface.

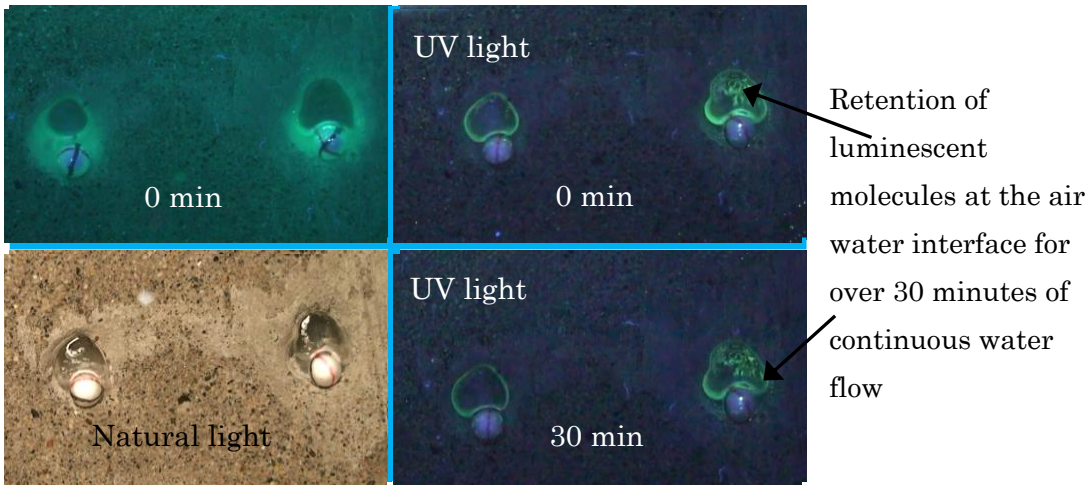


Figure 7-13: The nature of the surface of the trapped air bubble at 0 min when the green luminescent is supplied, how it appears in natural light a few seconds later, and 30 mins later under UV radiation and continuous tap water supply.

Either of these two possibilities supports the proposed hypothesis, and it is not yet possible to determine which of the two takes precedence.

7.5.5 Secondary molecular substitution at the air – water interface

The adsorption of luminescent molecules at the air – water interface has been observed under ultraviolet light. In addition, experiments were performed with other luminescent molecular solutions of different molecular configurations. Basically luminescent solutions of colours green, blue and red were used. Individual molecular adsorption of the different luminescent molecules at the air – water interface could be observed for each of them.

In addition, attempt was made to check the effect on an interface with already adsorbed molecules of addition of another luminescent solution. For example, if the interface presently has the green luminescent molecules adsorbed, what would be the effect of

adding a blue or red solution? When this was done, gradual substitution of the already adsorbed luminescent molecules could be observed. Or, failure to substitute an existing molecular layer could also be observed, depending on which molecular solution has a stronger interaction with the air – water interface.

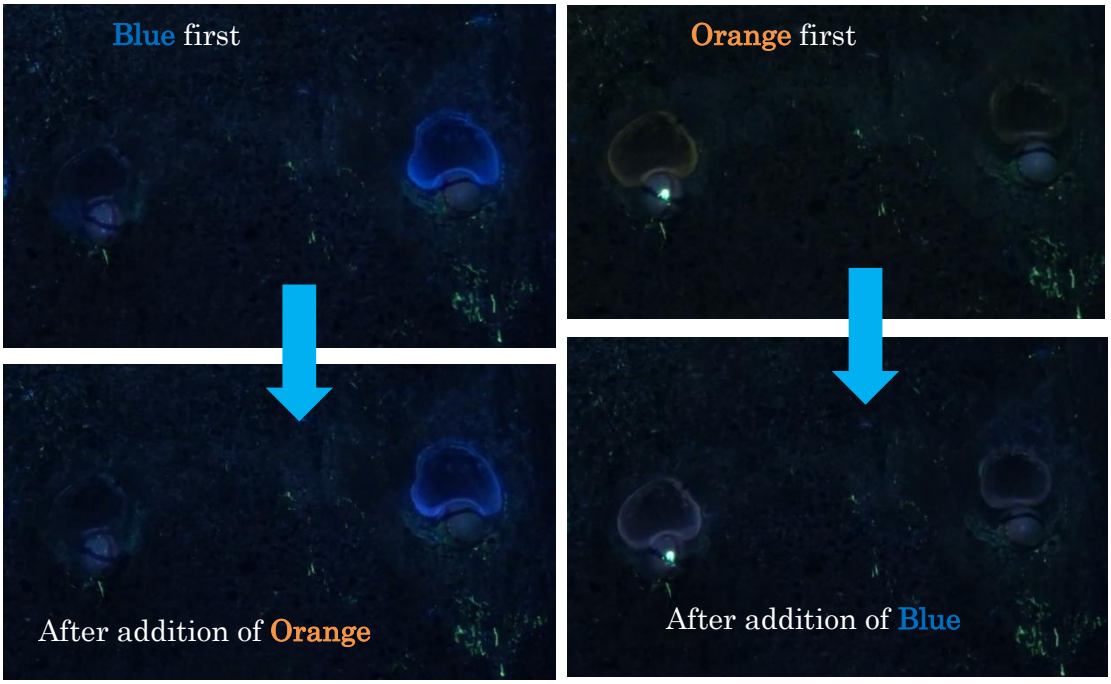


Figure 7-14: Molecular substitution/ rigidity at the air – water interface by different luminescent molecules.

Figure 7-14 shows molecular substitution and strength of different interfacial molecular adsorbents. The blue luminescent molecules have a stronger interaction with the air – water interface than the green and red (appears orange under UV light). On the left of Figure 7-14, the persistence of the blue luminescent is observed after addition of red or green luminescent; and yet when the red luminescent is adsorbed at the interface first (right of Figure 7-14), addition of the blue luminescent displaces it soon enough. The colour transition from orange to purple and eventually to blue can be observed in the process.

These observations reveal more about the nature of the air – water interface. Although the mechanisms of persistent adsorption despite continuous water flow at the interface are not clearly understood yet, they indirectly tell us that there is something unique about the nature of the air – water interface of surface trapped air bubbles within narrow gaps with water flow. It raises questions like; what are the luminescent molecules hanging on? Why aren't they washed out with the rest of the water flow? This

further reinforces our hypothesis that the air – water interface is made up of a fixed molecular arrangement that continuously supports the boundary between air and water.

Additionally, when we begin with an interface adsorbed with luminescent molecules (of whichever colour), addition of a surfactant solution quickly eliminates any colour at the interface! In these experiments soap solution was added to an already blue interface, and this caused disappearance of the blue colour. It is assumed that the surfactant molecules substitute the blue luminescent molecules at the interface. In effect, though not yet clear, water out flow rates are observed to increase. What is largely known is that soap molecules act to reduce surface tension in water, and this could lead to an increase in outflow rates. Or it could mean that the molecular rigidity at the interface is lost after addition of soap solution and the air – water interface can no longer play the water flow braking role! This effect is further verified by the spinning of the ball (see Figure 7-8) even when it is attached to an air – water interface, after addition of soap solution. As soon as the soap solution is added, spinning is observed to immediately start.

7.5.6 The rising air bubble study with luminescence

In section 4.7, air bubble rise in narrow interfaces has been tackled. In that case, the dynamics of a freely rising air bubble are not fully considered as wall effects interfere with the result – which is one interesting finding of this study. In this section, air bubble rise in a 100cm water column is performed, and with a different perspective.

A 100cm glass column of 10cm diameter is filled with a study liquid, in this case supersaturated tap water or diluted soap water (115g of soap to 20 litres of water), respectively. At the base of the glass column is a 1mm hole through which air bubbles are delivered by syringe injection. The released air bubbles at the base of the glass column are such that their interface is of luminescent molecules. The syringe contains a luminescent solution which is mixed with air and released in such a way that the released air bubbles have a luminescent molecular layer. The bubbles are released in supersaturated tap water and soap water respectively. Air bubble rise is recorded by video and also visual observation done. The whole set-up is carried out in a dark room with only Ultra Violet light provided. Figure 7-15 shows the experimental set-up adopted for this experimentation.

As the air bubble rises through water, several observations are made. In this experiment, based on the proposed hypothesis, an air bubble interfaced with

luminescent molecules should rise through the bulk liquid with the luminescent layer conveyed along with the air bubbles. This would be additional proof of the fixed nature of water molecules interfacing with air at the boundary with air. In the set-up where air bubbles were leased into tap water, the air bubbles were observed to convey the luminescence as they rise through the water.

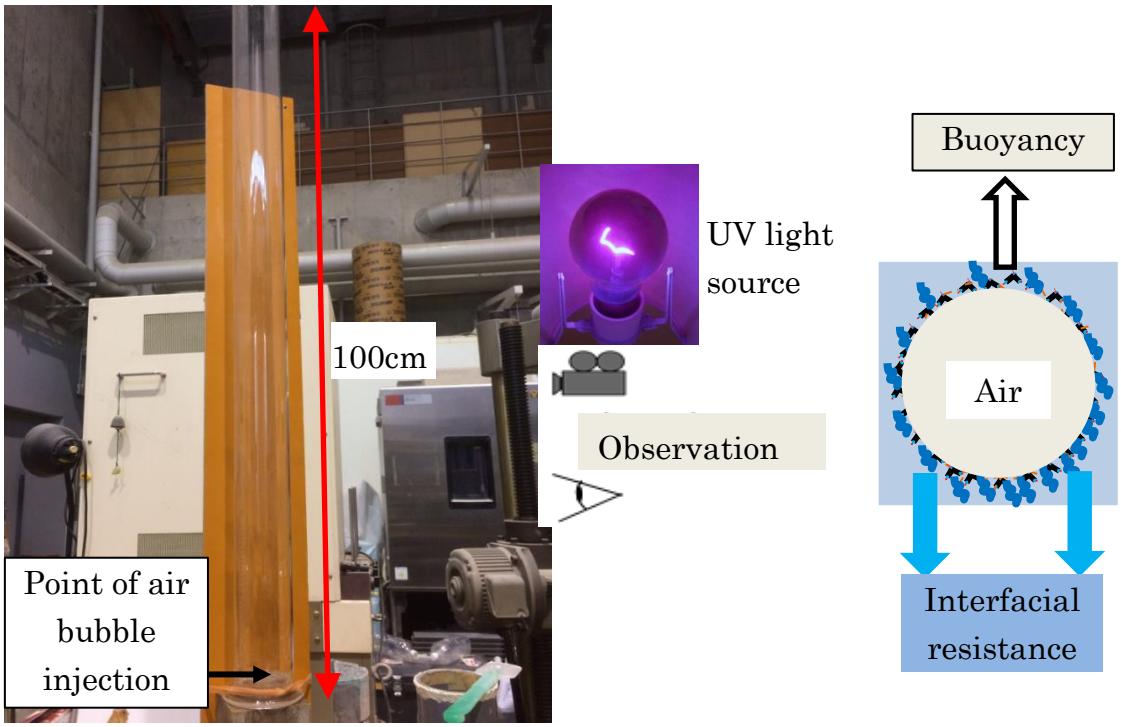


Figure 7-15: Experimental set-up to study air bubble rise through water column (left); illustration of air bubble rise through water (right).

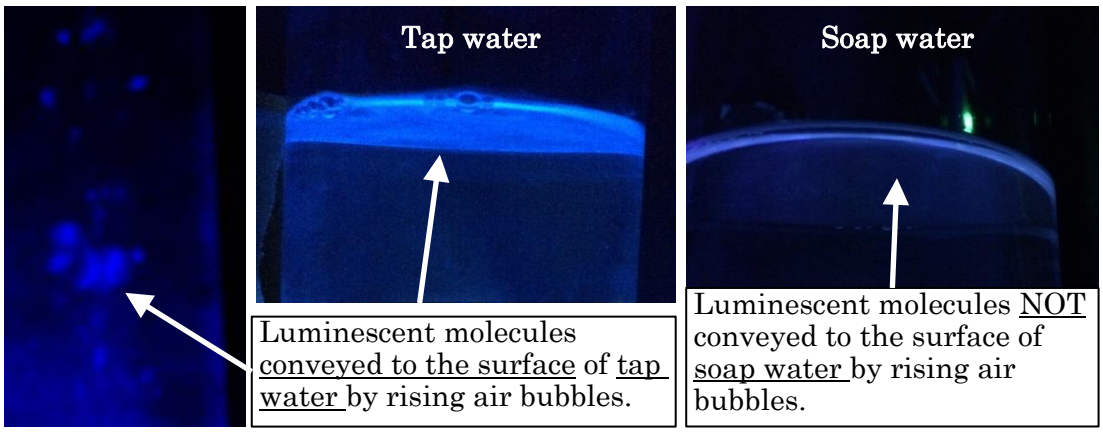


Figure 7-16: Observation of rising air bubbles (left), conveyed luminescent molecules at the water surface (center), and absence of noticeable luminescent molecular conveyance in case of soap water.

On the other hand, the set-up that used soap water as a medium through which air bubbles rose, the air bubbles could hardly be observed as they rose! The illumination provided by ultra violet radiation enables this observation to be done.

In the case of air bubble rise through soap water, as the air – water interface rises with luminescent molecules attached, dissolved soap molecules desorb them from the interface. Thus, we don't observe many of them conveyed to the surface of water at the top as shown in Figure 7-16.

In a related experiment of air bubble rise, where a normal air bubble is released in a glass column with surfactant solution [24], [25], a stagnant cap formation of surfactant molecules is formed at the base of the rising bubble as shown in Figure 7-17.

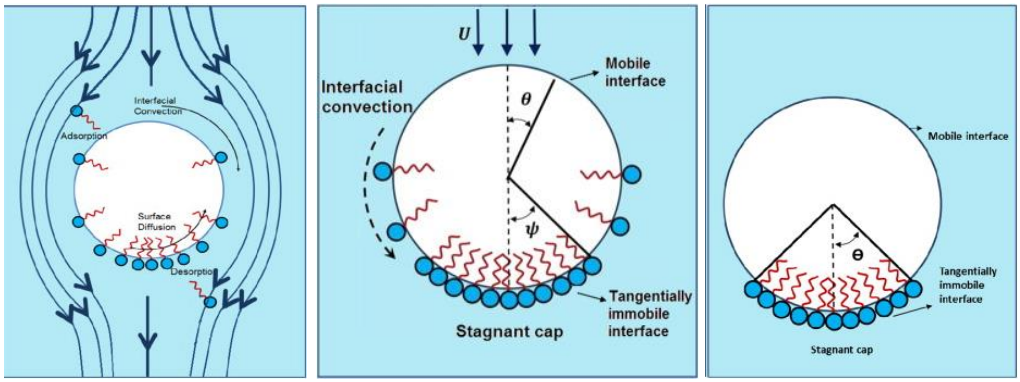


Figure 7-17: Surface concentration gradient caused by the convective flow around a bubble interface, and stagnant cap model for the surfactant distribution on the surface of a rising bubble.

Lotfi *et al* (2014) highlights the dynamics that occur at the interface as an air bubble rises. Desorption and adsorption of surfactant molecules at the interface occurs, leading to the development of marangoni stresses that lead to interfacial convection, eventually causing retardation of bubble motion. In contrary to this research, a stagnant cap could not be observed to be formed on rising air bubbles in tap water. A fully adsorbed luminescent air bubble surface is observed to be maintained as the air bubble rises through the water. It is thought that the different adhesion properties among the different molecules in both studies could be linked to the observed/expected differences.

Additionally, luminescent molecules were observed to be retained at the interface for over an hour despite continuous water flow on the surface of the bubble. On the contrary, soap molecules were observed to spend no more than 5 minutes at the air – water interface under the same conditions of continuous water flow. In this research however,

the mechanisms of molecular retention/adsorption and desorption are not discussed.

7.5.7 Understanding of hypothesis of rigid air – water interface

It has been hypothesized in this research that water molecules at the air – water interface assume a fixed molecular configuration, with restrained molecular rotation or spinning. This air – water interfacial characteristic determines the unique characteristics of water that are observed, especially in narrow gaps.

Regarding luminescent and surfactatnt molecular adsorption at the interface, it is rather the rigidity of water molecules at the interface that is hypothesized to maintain the surface adsorbed molecules/particles at the interface. Water surface molecules are implied to be strongly held compared to those in the bulk. This rigidity makes them less freely spinnable compared to those that exist in the bulk of water.

The freedom of spinning and rotation at the interface gradually increases as one moves away from the interface and into the water bulk. Figure 7-18 illustrates the effect of restrained interfacial water molecules.

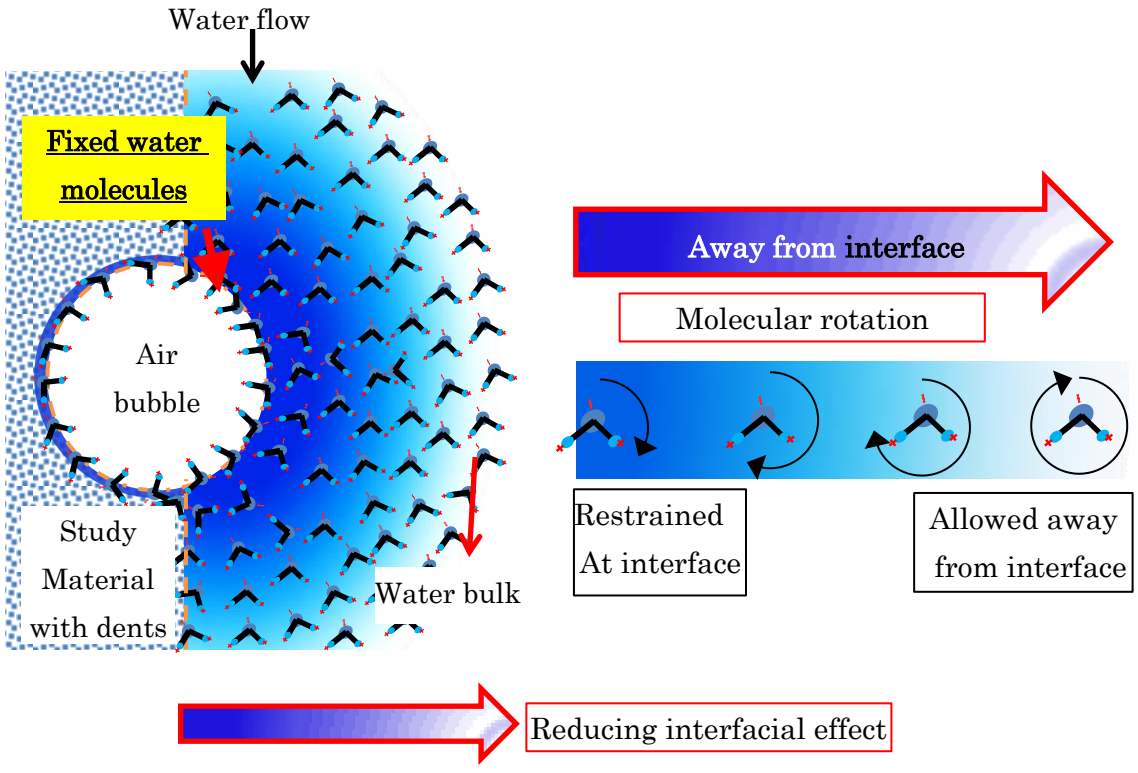


Figure 7-18: Illustration of the air –water interfacial effect in narrow gaps with continuousl water flow. Water molecular spinning and rotation is restricted at the interface but gradually released away from the interface and into the bulk.

Surfactant molecules once adsorbed at the interface tend to reduce surface tension, and this is common knowledge. Their presence at the interface removes the imbalance in surface water bonding. Figure 7-19 illustrates the effect of surfactant molecules at the water surface, and how they break the surface energy imbalance that exists.

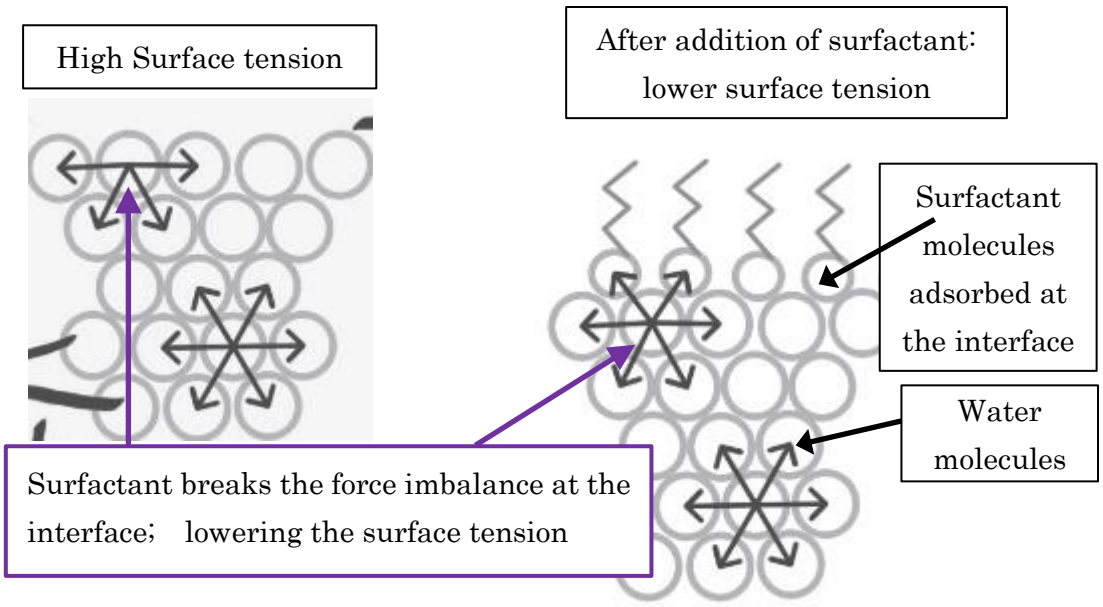


Figure 7-19: Illustration of surface phenomenon with and without surfactant molecules. Presence of surfactant molecules greatly reduces surface tension.

While interfacing with air, there is no recognisable adhesiveness with air molecules; this is the cause of the large surface tension of water. On the contrary, when water comes in contact with hydrophilic solid surfaces, there is some level of adhesiveness between water molecules and liquid molecules. The presence of this interaction between the two brakes the strong cohesiveness at the water surface. This difference between the two scenarios is what is responsible for the observed water flow reduction courtesy of the braking mechanism of flow surface anchored or fixed micro and nano air bubbles.

In the initial stage of water supply and flow, there largely exists the solid – liquid interface. Once the conditions favourable for air bubble growth are attained, and air bubbles start growing, the air – liquid interface comes into play and its associated effects become relevant depending on the relative gap size and effective air – water interfacial zone.

The water flow braking mechanism arises from this newly created and growing interface – the air – water interface! It is quite clear from observations and measurements of water flow that the air – water interface is lined by water molecules

that strongly held in position and to each other. Figure 7-20 illustrates the difference between solid – liquid and air – liquid interfaces. Minus the formation of the air – liquid interface, water flow would be expected to remain steady without varied flow rates as long as other conditions are kept constant.

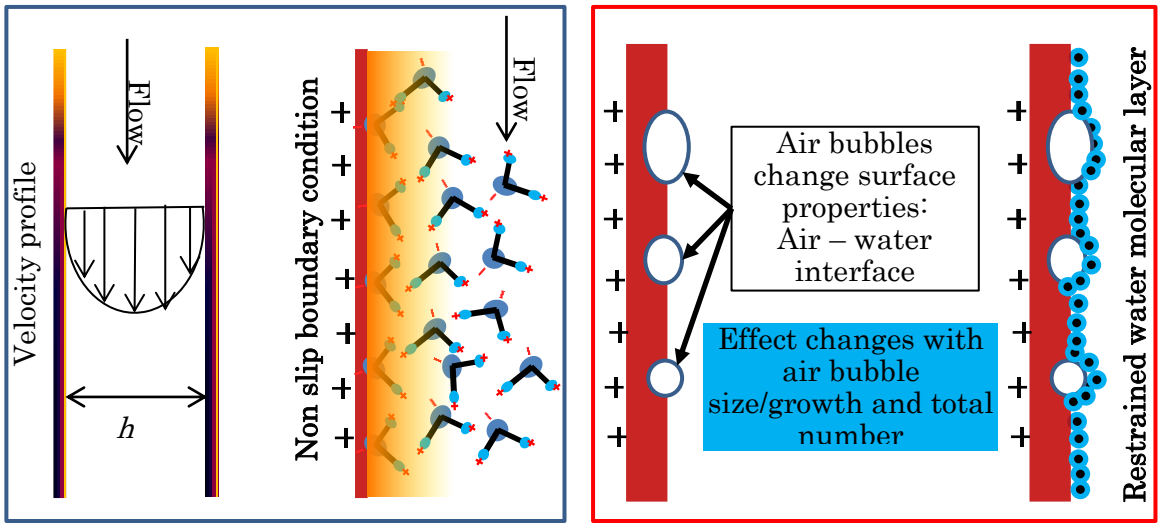


Figure 7-20: Illustration of boundary condition and change of surface characteristics due to formation of fixed micro and nano air bubbles. The surface over which water flows is now of liquid – solid and liquid – gas interface.

The proposed hypothesis has assisted in clarifying the mechanisms of water flow reduction in narrow gaps in the absence of large visible air bubbles. For air bubble growth observed in conditions of continuous water flow, and not observed under static water conditions, the dynamics of this hypothesis clarifies this. Under static conditions, and for an air – water interface, it becomes clear why an air bubble grows in flowing supersaturated water – air transport to the interface is faster, and much slower in the case of static water conditions.

There is a zone of influence stretching from the boundary with air and into the bulk water. The size of this zone is not exactly known, but is expected to be a standard size under certain specific conditions. Molecular rotational translation occurs in this region, until a point where rotation and spinning speeds are constant throughout the bulk. In this research, attempt has been made to estimate a practical size or region of influence of this rigid interface, in section 7.6.

7.5.8 Effect of soap solution on water flow in narrow gaps

The effect of soap solution has been observed with the spinning floater ball, and how it

leads to loss of anchorage causing the initially restrained ball to spin. This occurs because the initially well cordinated hydrogen bonding in the interfacial layer becomes broken by the adsorption of surfactant molecules. Once the hydrogen bonding is broken, lubrication at the interface is enabled.

In this research, in order to investigate further the anchorage mechanism of fixed micro and nano air bubbles, equilibrated water is initially used, and water flow reduction is observed in the absence of any visible air bubbles. After this, a dilute soap solution is substituted as the source of water. Figure 7-21 shows the results of this experiment; water flow reduction occurs initially, and as observed in this research, it is due to the fixed micro and nano air bubbles on the surface of water flow. Once dilute soap solution is added to the specimen, water flow amount is observed to increase immediately. This increase in water flow is due to the un-anchoring mechanism due to either presence of soap molecules at the interface or it's washing out of the previously fixed micro and nano air bubbles.

Soap solution is observed to act in possibly two ways;

1. When soap molecules adsorb at the air – water interface, they remove the imbalance in bonding at the air – water interface. Once this imbalance is removed, surface tension is immediately reduced. This is what affects the rigidity at the interface; surface lubrication is enhanced increasing water flow amounts.

2. After adsorbing at the interface, the air bubble may become unfixed, and this causes it to be easily and quickly washed out of water. Once this happens, the previously water braking effect is removed. In this case, water flow amounts increase immediately. In the case where large water flow blocking bubbles exist, addition of soap solution unhinges them as well and get them washed out with the water flow. Figure 7-21 shows the effect of soap solution on a set-up of decreasing water flow using equilibrated water condition. A sharp rise in the flow amount is immediately observed after supply of soap water.

The mechanisms of soap molecular adsorption and interaction with the interface have been studied by several other researchers [24], [25]. Therefore in this research, the dynamics of soap molecular adhesion are not explored. It's only the understanding of their mechanisms and behavior that is employed in this research. For example the knowledge that soap molecules lower the surface tension of water. In Figure 7-21, it is depicted (inset) of the possible soap molecular adsorption at the interface and how it would disorganise the orderly hydrogen bonding at the air – water interface. In addition,

the hydrophilic and hydrophobic properties of soap water are further utilised in the understanding of this research.

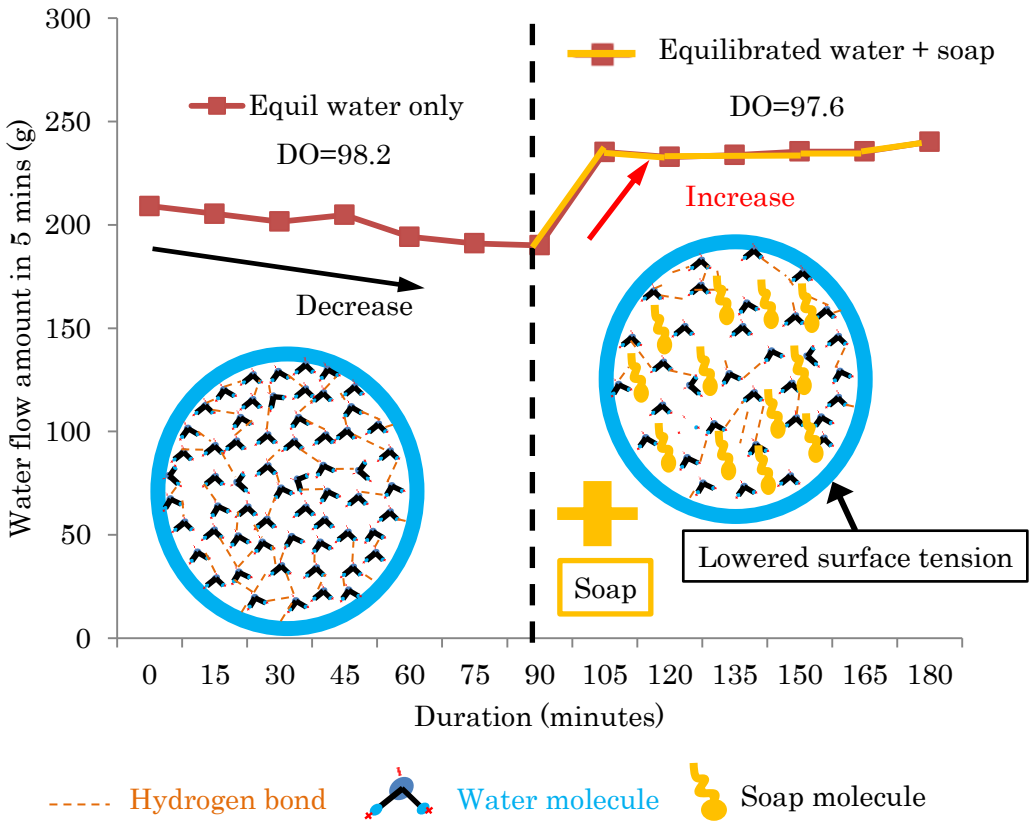


Figure 7-21: Water flow graph using equilibrated water and later with soap diluted equilibrated water. The effect of un-anchoring mechanism of soap water is observed when dilute soap solution is added.

The observations made with and without soap solution reveal behaviours that depict the true nature of water's surface. These indirect observations further point to the fixed arrangement of water molecular layers at the air – water interface. Once this arrangement is broken by the adsorption of soap molecules, anchoring and thus water braking effect is lost.

7.6 Investigation of the size of the fixed water layer at the interface

With luminescent adsorption at the interface further reinforcing the presence of a fixed thin water layer, it was important to attempt to determine its thickness. How far does the fixed water molecular structure extend into the bulk liquid? Of most relevance is how many molecular layers are causing this kind of behaviour.

Luminescent molecular adsorption means that molecules this big can be entangled into

the interface. A rudimentary approach was used to estimate the size of this layer indirectly. In the preparation of a luminous solution, its paint is first dissolved in water and then filtered. The filtrate is collected and used for tests with the interface. Two approaches were used to estimate the possible size of the interfacial layer that maintains luminescence.

7.6.1 SEM image analysis for trapped luminescent particles

When a dilute luminescent paint solution is filtered with a grade 2 filter paper, some of its residue is trapped at the surface of the filter paper. With this residue, the minimum particle size of luminescent paint can be measured by scanning electron microscopy. In reality this only represents the minimum size for the trapped residue since much smaller particles are what is collected in the filtrate. None the less, this approach gives a rough estimate of the possible size of the fixed layer, about 250nm. Figure 7-22 shows SEM images of luminescent particles trapped on a filter paper. Particle shape is spherical.

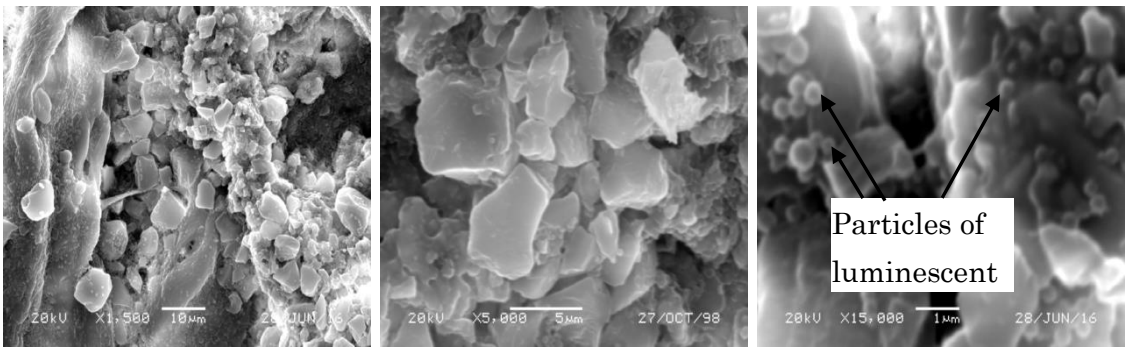


Figure 7-22: Scanning Electron Microscope (SEM) images of luminescent particles on a filter paper (images taken with the help of Prof. Goto, Kishi Lab, IIS)

7.6.2 Maximum water spread between two parallel glass interfaces

Another crude method was used to attempt to estimate the size of the luminescent particles that could be trapped or adsorbed at the air water interface. After the filtrate was collected, a drop of the solution is placed on a clean glass plate, and another glass plate used to compress it and cause it to spread. A slight pressure is applied on the parallel set-up until a maximum spread is achieved. Under UV light, and while still pressing on, the size of the circular patch is marked on the glass plate (radial diameters can be measured). The volume of the drop is known, plus the mass. With these dimensions, the maximum size of particles trapped between the plates can be estimated. Figures 7-22 and 7-23 show an illustration of this technique, and actual observations

during the experiment.

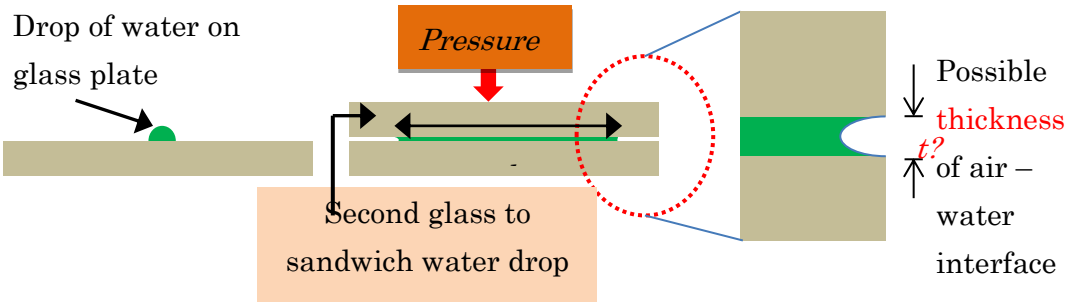


Figure 7-22: Determination of the minimum possible thickness of water trapped between two glass plates.

Table 7-23 shows the computation of particle sizes. An average size of 3.5 microns was measured as the maximum particle size of luminescent that could be trapped in this fixed water layer at the interface. This is 15 times larger than that measured by SEM technique, but probably gives a range of the possible sizes. It is not only these nano and micro sizes of luminescent particles that are adsorbed at the interface; their molecular constituents too do the same in their individuality.

Water molecules are so much smaller than these luminescent particles, and are probably existing is special clusters at the interface to be able to pull off this kind of effect.

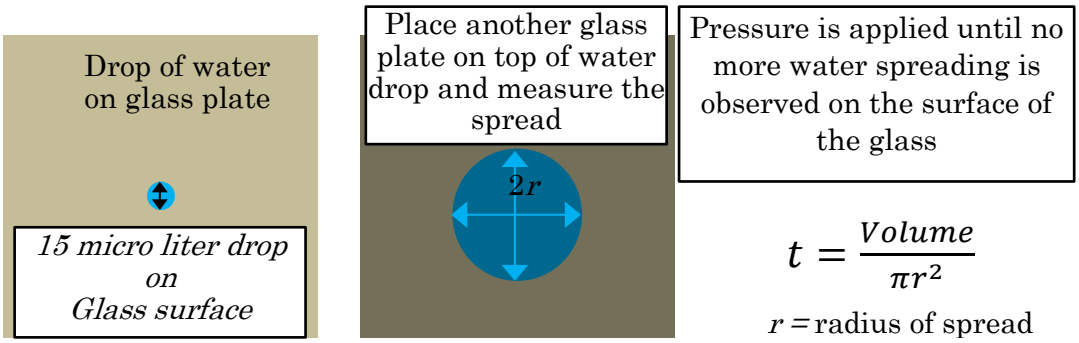


Figure 7-23: Computation of minimum thickness of water trapped between two glasses, by measuring the maximum spread on the surface

Table 7 - 1: Measurements to determine thickness of water and luminescent solution between two glass plates

Water, Avg: 3.408 micro				Water + Luminescent, Avg: 4.419micro			
d_1 *(mm)*	d_2 *(mm)*	*r (mm)*	*t* micro	d_1 *(mm)*	d_2 *(mm)*	*r (mm)*	*t* micro
67	70	34.25	4.070	75	68	35.75	3.736
65	62	31.75	4.736	78	73	37.75	3.350
64	67	32.75	4.452	75	81	39	3.139

7.7 Chapter summary

In this chapter, the air – water interface is investigated and the traditional understanding of surface tension brought to question. It has been clarified that it is difficult to explain some of these observations at the air – water interface with the surface energy approach of surface molecules; that instead, a microscopic theory of the nature of the interface is necessary to explain some of these deviant observation due to the nature of the interface.

Thus, a hypothesis about the structure of the air – water interface has been proposed to explain the observations made. Supporting indirect evidence of the fixed interfacial water molecular layer has been put forward through experimentation with several approaches. It is still not enough evidence, and more investigative research needs to be done to clarify on the exact nature of the air – water surface.

The indirect evidences show that the air – water interface behaves like a rigid surface during water flow through narrow interfaces. This rigidity implies that water molecular rotation/spin is much more restrained at the interface and this rigidity gradually reduces away from the interface. This means there is a region/zone of influence of this effect and is strongest at the air – water interface.

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Chapter 8 Conclusions and Recommendations

This research has investigated water flow in narrow gaps of concrete surfaces bound to a glass plate in order to visualise flow through such narrow gaps as would be in closed concrete cracks. An experimental investigation of water flows rates, direct visual observations of air bubble formation, a side by side review of existing literature, plus a focused investigation approach form the basis of these conclusions and recommendations.

8.1 Conclusions

- Water flow in narrow gaps of concrete (< 0.3mm) has the potential to breed air bubbles that would stay anchored within the cracks. The quality of flowing water (supersaturated with dissolved air or not) will determine the extent of air bubble growth. Other than concrete, other materials too with relatively rough surface characteristics are capable of causing air bubble growth when bound in narrow gaps.

- Once an air bubble is anchored within the wall of water flow in a narrow gap, it will start growing under the necessary condition of supersaturated and moving water. The growth of an air bubble involves air exchange at the air – water interface. Water movement ensures a constant supply of air-rich water at the interface. The surface of attachment provides a firm fixing position, and the narrow gaps help to maintain stability of the bubble.

- The created air bubbles are very stable and persist as long as there is water flow within the gaps, and ambient conditions of temperature and pressure remain relatively constant. Unlike the expectation that water flow would wash them out, these air bubbles are strongly anchored either on the walls of water flow (when still small), or between the walls (when big and stretch across the path of water flow).

- Previous understanding of water flow reduction due to air bubbles was understood to be the result of water path blocking mechanism; it has now been clarified further that, initially, when the bubbles are small (of micro and nano sizes) they cause notable water flow reduction by the braking mechanism. Even though the effect of these finer air bubbles is not so big in sub-millimeter scale gap sizes, it is expected to be much more magnified for micro or nano scale gaps of water flow, such as in the dense micro pore structure of concrete or microfluidic devices involving water movement.

- The braking mechanism of water flow in narrow gaps is linked to the nature of the air water interface. A hypothesis describing the nature of the air – water interface for surface fixed air bubbles in the narrow paths of water flow has been proposed. It is hypothesized that water molecules at the air – water interface of these said bubbles take on a fixed molecular arrangement which offers them restrained rotational ability compared to other water molecules in the bulk. A direct visual observation technique under ultra violet light, of the air – water interface with adsorbed luminescent molecules has revealed the over one hour retention of these surface molecules until continuous water flowing conditions. This, in addition to other indirect proofs strengthens this hypothesis.

The mechanisms of water flow in small spaces or close to interfaces have attracted a lot of attention among several researchers recently; at the same time, the works of these researchers are quite divergent on certain issues, though quite convergent on others too. Additionally, we recent advances in technology, researchers are recently able to make more revealing observations and perform experiments that prove earlier areas of scientific contentions about the nature of the air – water interface. What is largely agreed upon is that the air – water interface is complex and elusive, and yet it plays a significant role in determining a great range of functionalities. Water itself is unique, with properties not expected of a molecule of its molecular weight, and able to exist in three different phases. There is no conclusive evidence regarding the nature of the air – water interface; there are however plenty of conflicting indirect evidences regarding the true mechanisms of the water surface

8.2 Recommendations and future works

Based on the findings of this research, the following recommendations and future works are stated.

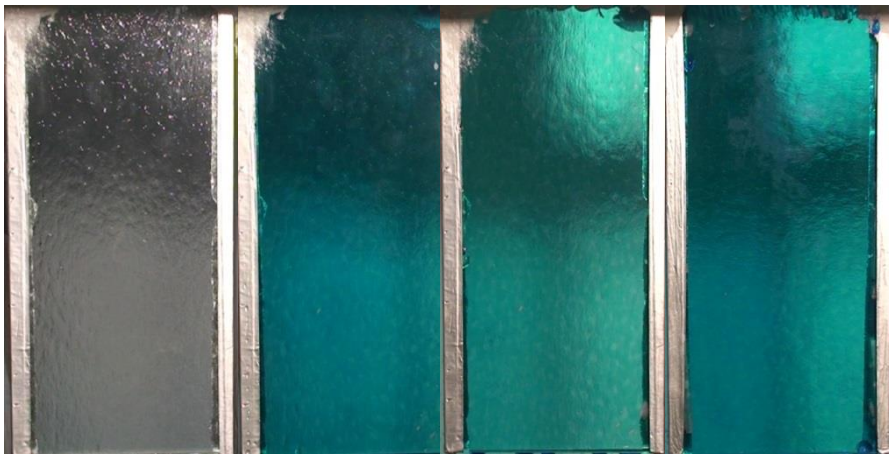
- Water flow measurements through narrow gaps such as in concrete cracks lead to the creation of air bubbles that significantly choke water flows. It is thus recommended that water flow measurements critically take into consideration the existence of this effect, for example by avoiding the use of supersaturated. In self-healing concrete testing especially, the use of supersaturated water should be avoided completely, and a minimum crack width of 0.3mm adopted.

- The mechanisms of water flow braking have focused on the nature of the air – water interface. Several indirect proofs concerning the nature of the air – water interface have been gathered, but there is need for additional supporting evidence to further verify the hypothesis that water molecules at the air – water interface

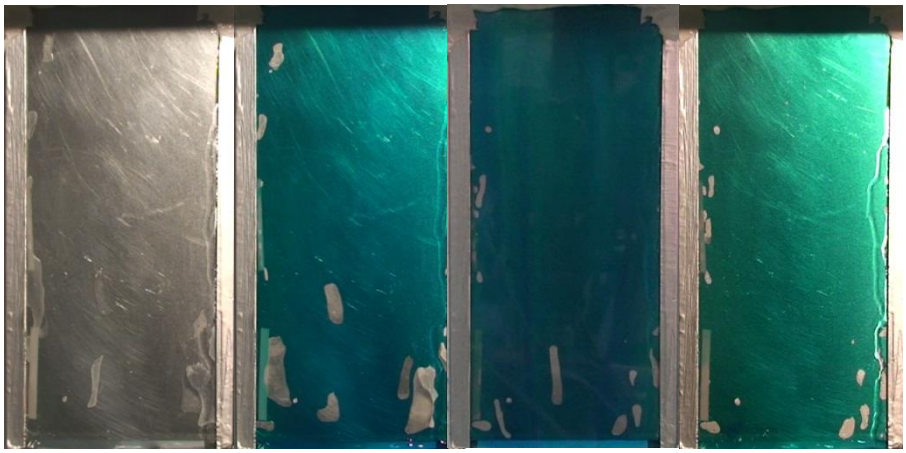
are fixed in position compared to those in the bulk.

- Practical applications of some of the findings of this research have not been deeply investigated. Since the results of this research directly redirect our understanding of water permeation mechanism, it is recommended that the practical implications be investigated for example with water permeation into concrete. For example it is well known that surface tension of water influences water permeation directly; it has also in this research been observed that reducing surface tension of water by adding surfactants, actually affects the nature of the air – bubble interface.

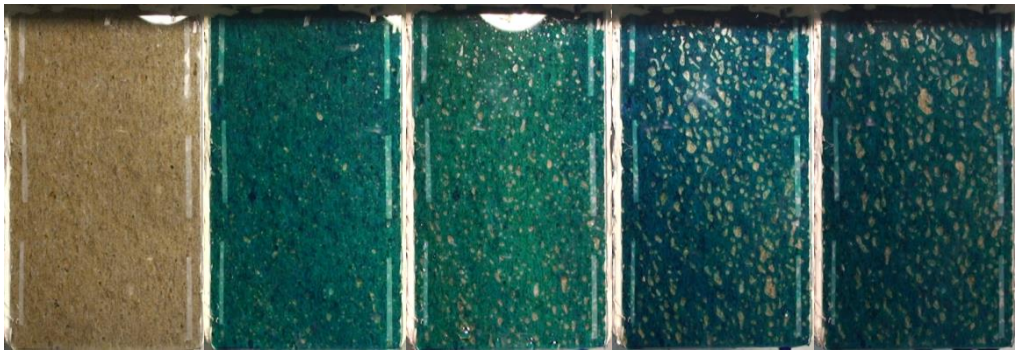
Appendix



Images showing result of using frosted glass bound glass - glass

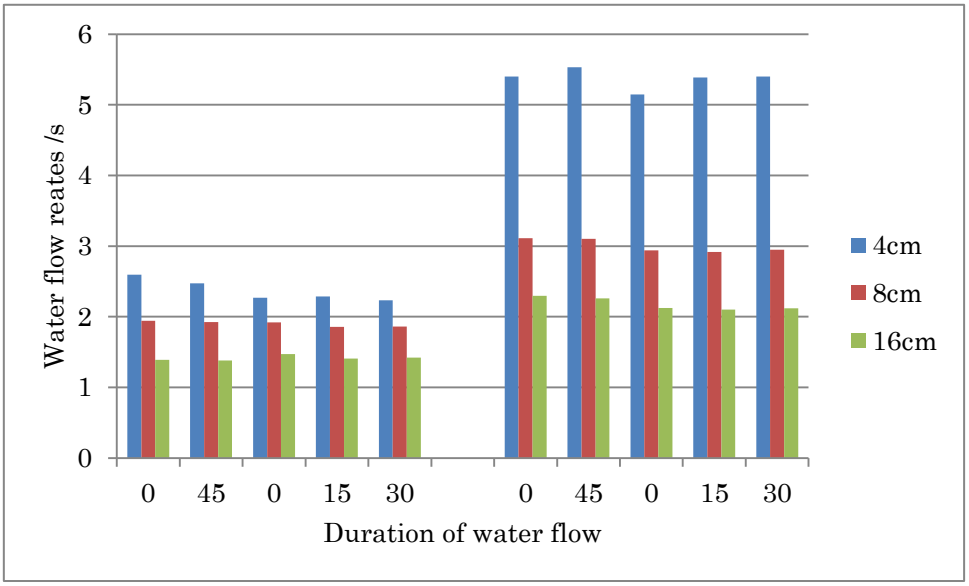


Images showing result of using Plain Aluminium plate bound to plane glass

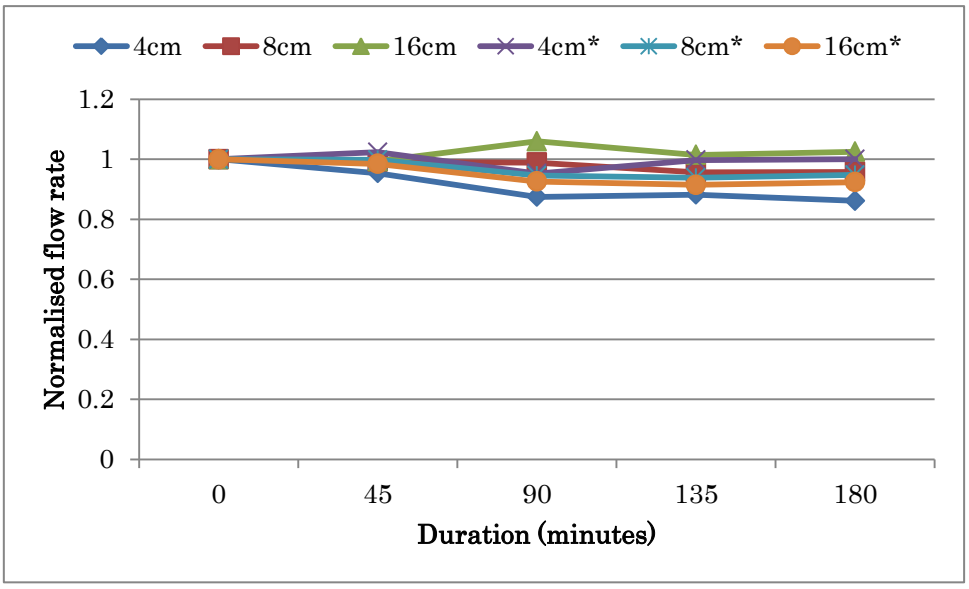


0h 3h 5h 7h 3 days

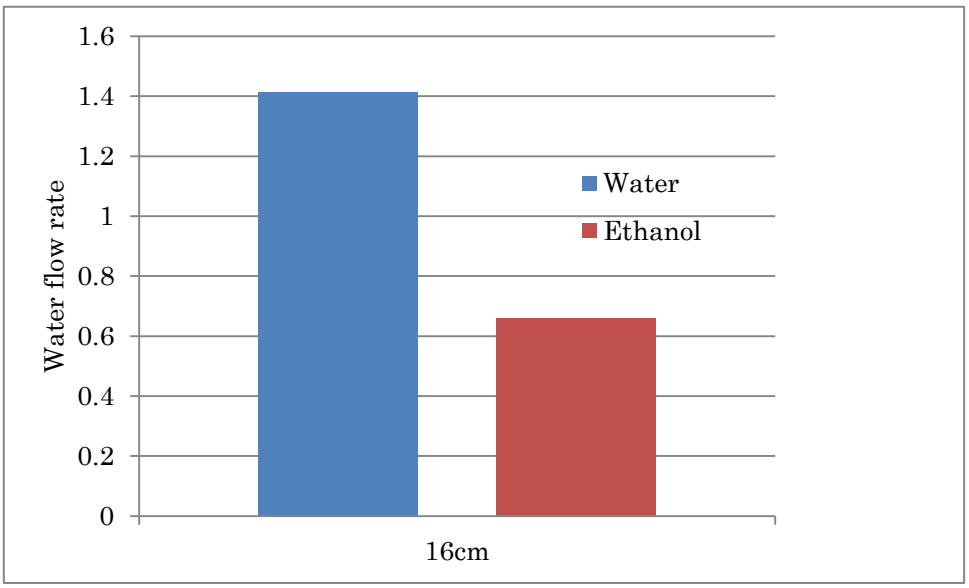
Images showing result of pumice bound to plane glass



Water flow results for glass – glass specimens for two water heads regimes

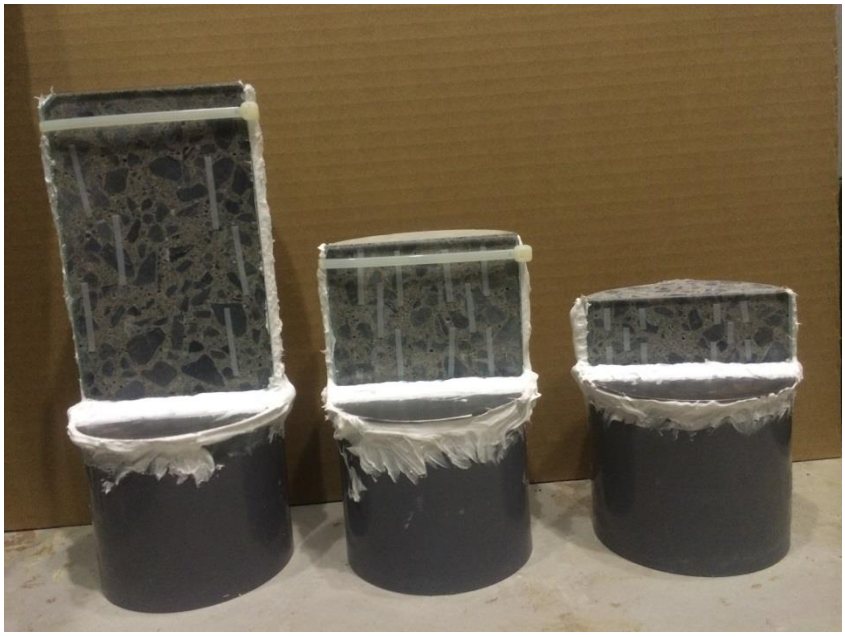


Normalised water flow results for glass – glass specimens for two water regimes

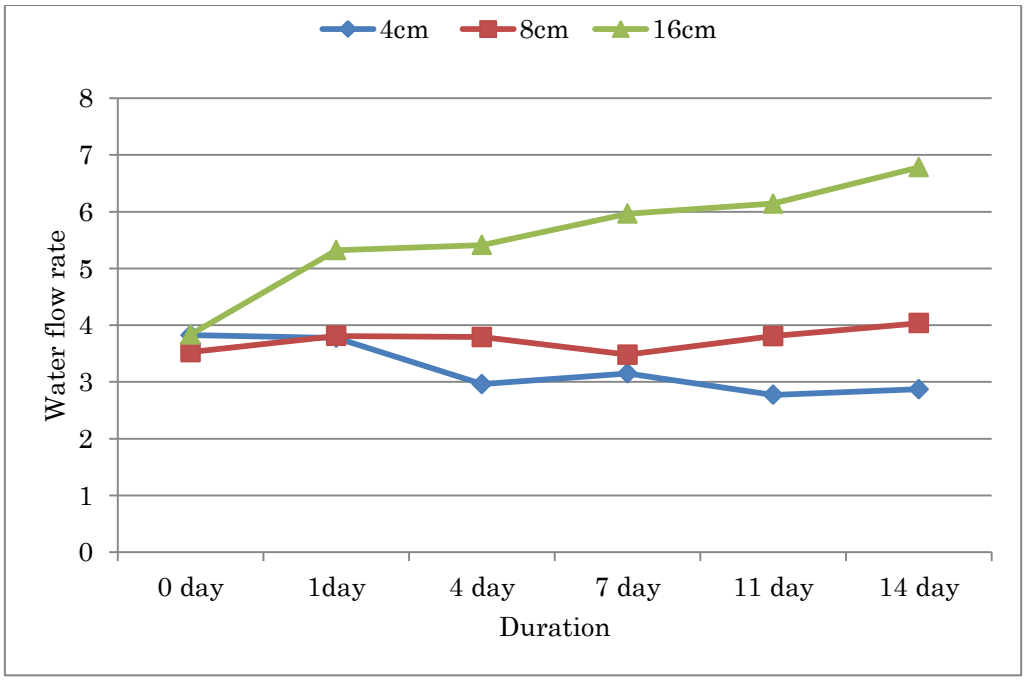


Water flow rate for glass – glass of ethanol Vs water for a standard specimen

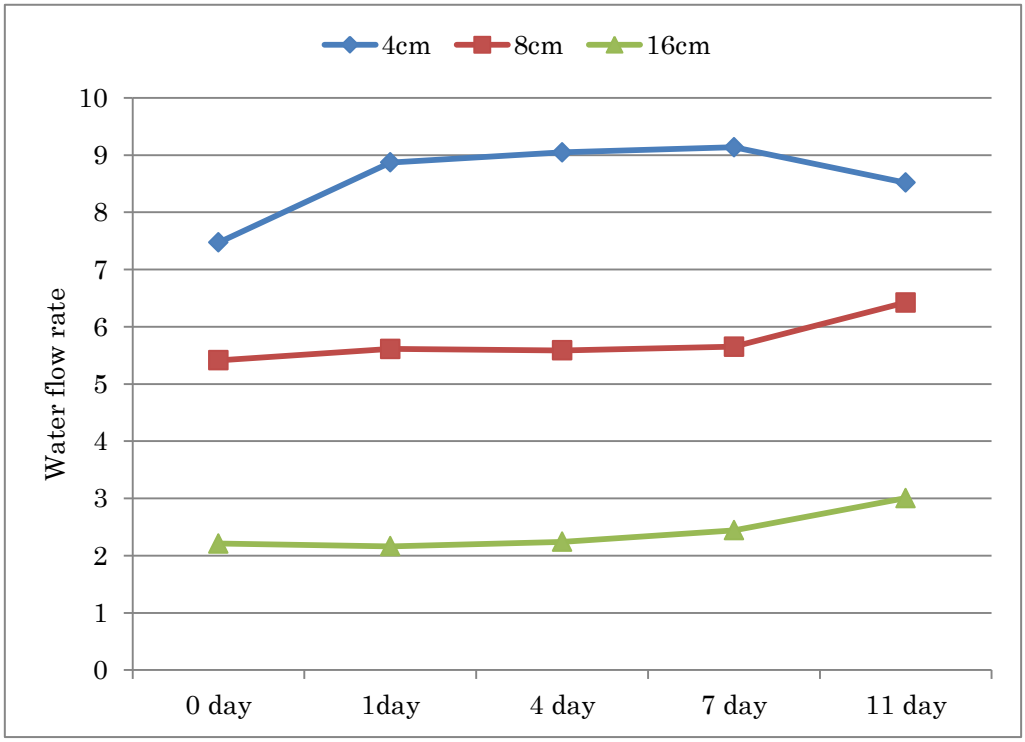
Image of ethanol flow for glass – glass specimen



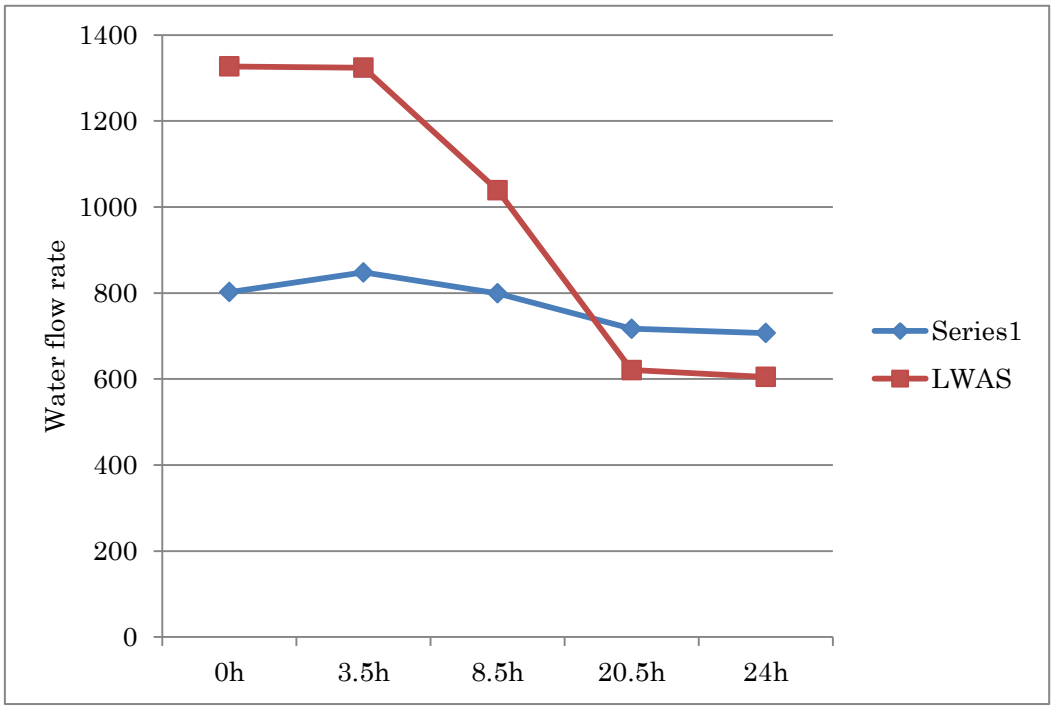
Concrete – Glass specimens of different sizes to check effect of water flow



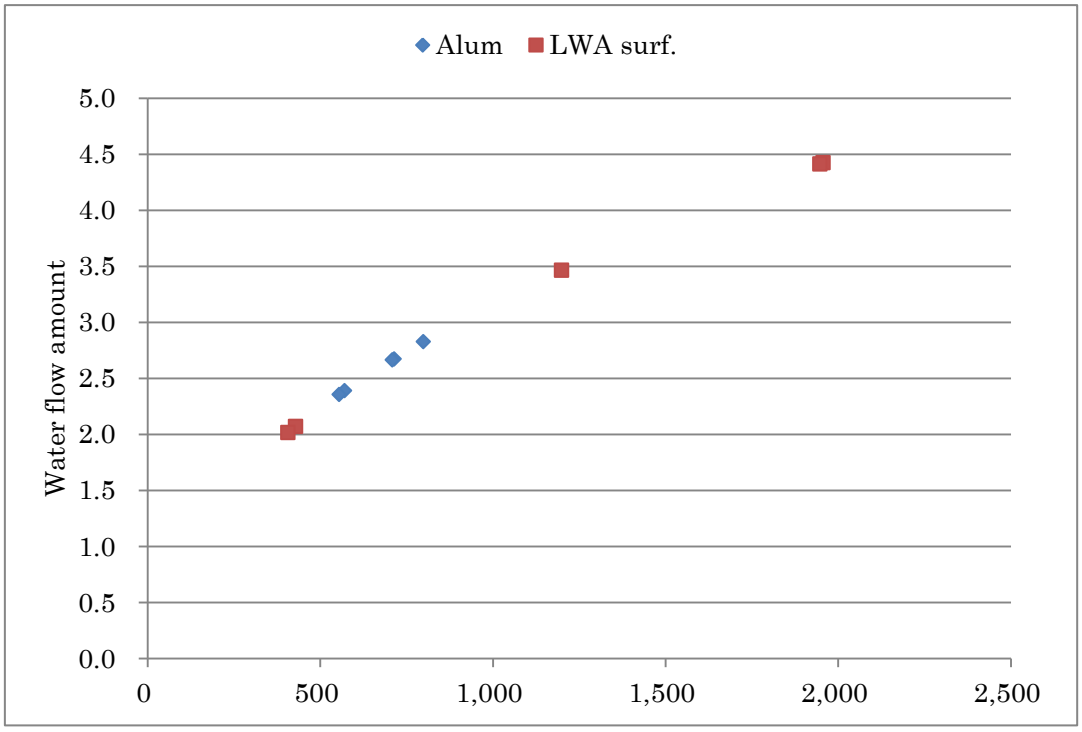
Water flow results for Concrete – Glass specimens of different hydraulic head



Water flow results for Glass – Glass specimens of different hydraulic head



Comparison of Light weight aggregate surface and aluminium surfaces effect on water flow



Cumulative water flow for aluminium and light weight aggregates

10/23/14	① aluminium(water from high position), falling height		②aluminium (water from low position), falling height		③Pumice (water from high position), falling height		④Pumice (water from low position), falling height	
	water flow (g)	comments	water flow	comments	water flow (g)	comments	water flow	comments
0h	802	No bubbles		No bubbles	1327	No bubbles		No bubbles
0.5h		very small/few		very small(bigger than ①)/few		very small/few		very small/few
1h								
1.5h		very small/increase near the bottom		small air bubble increase				small air bubble increase
2h						bigger/ increase overall		
2.5h								bigger/ increase overall
3.5h	848	bigger/ increase gradually to top			1324			
7.5h				bigger/ increase				bigger/ increase
8.5h	799	bigger/start to increase near the top			1039	many air bubble overall		
20.5h	717	bigger/ increase everywhere			621			
24h	707			bigger/ increase	605			bigger/ increase

Typical visual observation comments during water flow observations of specimens

No. of air bubbles	Area	Mean	Min	Max
1	433	190.855	128	232
2	185	179.286	128	224
3	658	205.617	128	248
4	434	217.327	128	248
5	477	212.143	128	248
6	285	204.295	128	248
7	81	161.481	128	200
8	278	174.849	128	224
9	231	188.468	128	240
10	30	147.2	128	168
11	501	189.142	128	232
12	660	171.697	128	232
13	99	165.253	128	200
14	228	195.895	128	248
15	448	209.036	128	248
16	401	179.571	128	232
17	520	193.985	128	248
18	425	195.953	128	248
19	271	199.97	128	248
20	350	190.491	128	232
21	159	183.346	128	224
22	412	186.35	128	224
23	426	201.84	128	248
24	260	179.385	128	240
25	506	198.277	128	248
26	289	187.875	128	240
27	676	198.994	128	240
28	175	195.749	128	232
29	361	197.208	128	232
30	545	198.385	128	240
31	610	189.718	128	232
32	14	138.857	128	152
33	641	192.624	128	248
34	195	181.005	128	232

35	593	210.604	128	248
36	22	147.636	128	176
37	268	189.045	128	232
38	902	198.137	128	248
39	473	205.564	128	248
40	239	191.598	128	232
41	167	183.856	128	232
42	413	179.177	128	232
43	415	199.634	128	248
44	244	187.016	128	248
45	377	195.247	128	240
46	652	200.16	128	240
47	379	208.042	128	248
48	578	200.886	128	240
49	69	185.739	128	232
50	170	181.224	128	232
51	472	167.169	128	232
52	613	219.915	128	248
53	543	189.068	128	216
54	204	199.608	128	240
55	555	217.139	128	248
56	858	197.277	128	248
57	281	189.779	128	232
58	215	184.037	128	224
59	3	130.667	128	136
60	1	128	128	128
61	81	183.407	128	248
62	90	181.511	128	216
63	53	188.377	128	248
64	49	172.898	128	224

Unsaturated Initial Condition, Image analysis output data; ImageJ

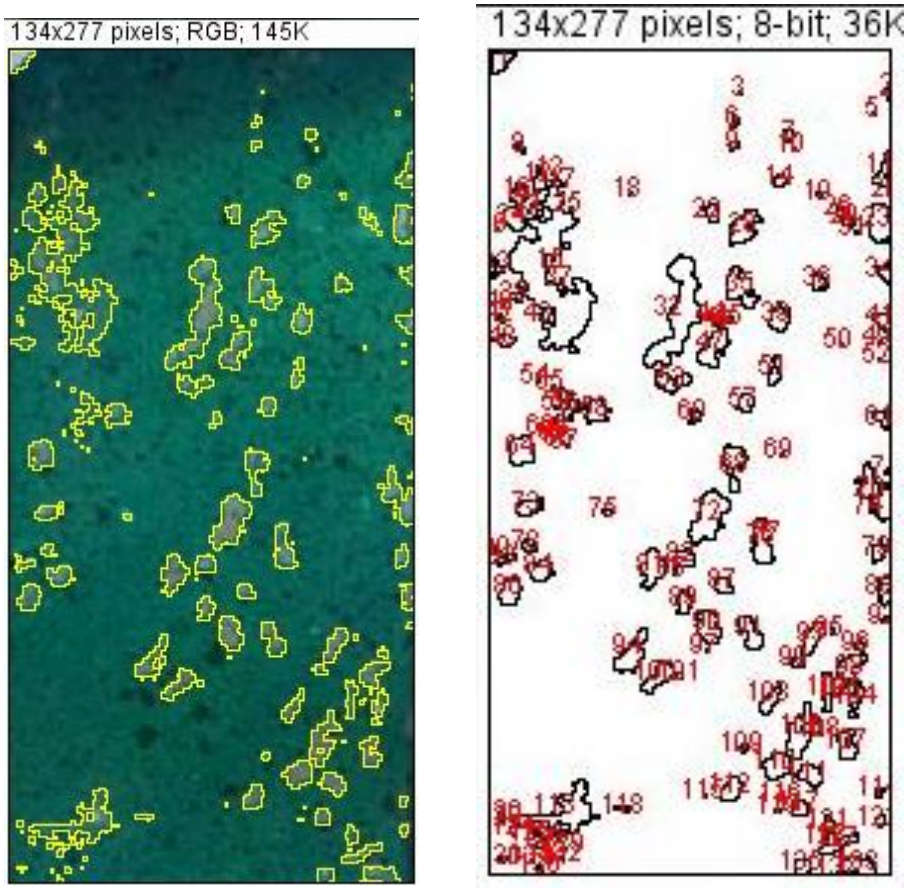
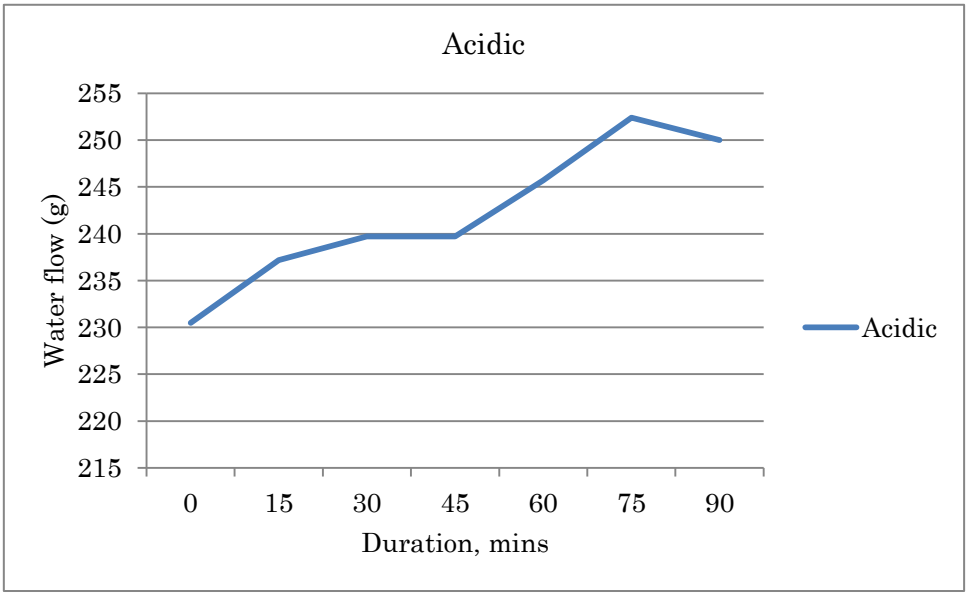


Image analysis by ImageJ and air bubble size computations

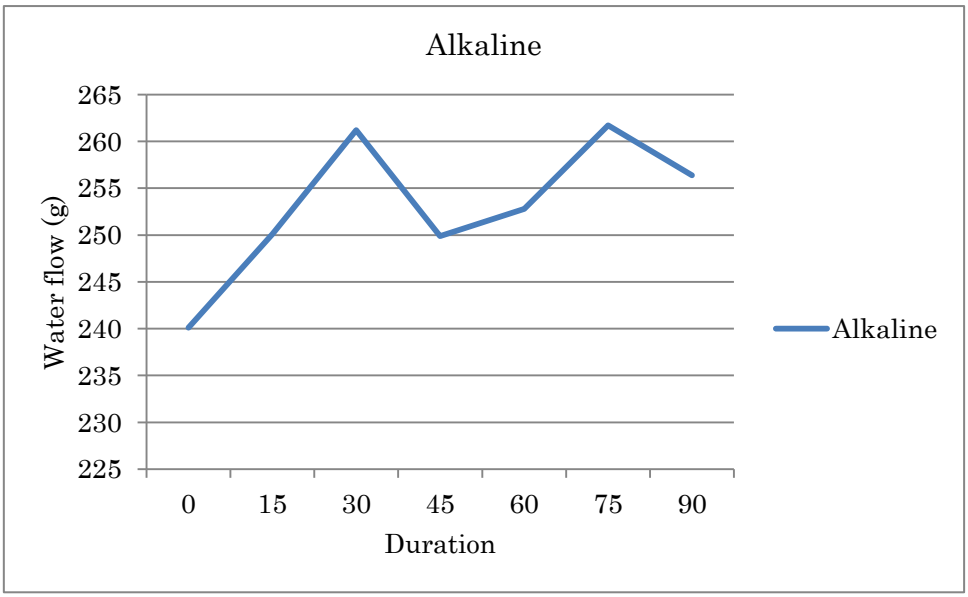
Image analysis by ImageJ and air bubble size computations

Concrete	Spec 1		Spec 2
Time	**slow flow**		**fast flow**
0	42		1097.9
15	40.6		1074.3
30	42.9		1110
45	38.6		1108.1
60	39.6		1100
75	38.5		1095.3
90	37.8		1108.5
105	34.5		1053.5
120	34		1081.4

Concrete	Spec 1		Spec 2
Time	**slow flow**		**fast flow**
0	41.7		1184.7
15	40.7		1120.5
30	43		1144.7
45	42.1		1113.2
60	39.1		1067.7
75	37		1001.9



Flow rate of degassing using acidic unsaturated water



Flow rate of degassing using alkaline unsaturated water