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Observations of air-bubbles escaped from fresh cement paste

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ABSTRACT

Recent experimental work is presented using a new technique to observe bubbles that have escaped from cement pastes and suspended in the bleed water. These experiments suggest that the stability of an air-entrained bubble may be related to the integrity of the hydration shell. This paper also reviews literature dealing with changes to air bubbles with time in fresh air entrained cement paste and concrete and to the existence of a shell surrounding these bubbles.

1. Introduction

Development of an air void system in hardened concrete through the use of an air entraining admixture (AEA) to stabilize air bubbles in fresh concrete is the primary method of producing freeze–thaw-resistant concrete. Although AEAs are widely specified and used to obtain frost and salt scaling resistance, practitioners still face significant problems in reliably and reproducibly stabilizing and maintaining an effective air-void system in concrete. Existing literature, based on laboratory and field observations, suggests that all aspects of the concrete construction process can affect the air void system in concrete [1]. In addition to the influence of dynamic processes such as batching, mixing, transporting, placing, consolidating and finishing the concrete, it has been reported that air bubbles in fresh concrete can change while the plastic material is at rest [2,3]. This paper reports several experimental observations of air bubbles that have escaped from cement paste and observed over time.

The goal of this paper is to resolve some of the conflicts presented in previous research, which are reviewed in Section 1.1 of this paper. This was achieved by developing a new experimental method that uses microscopy to examine the changes in bubbles separated from 0.42 w/cm paste. While these observations are not numerous enough to obtain a complete understanding of the behavior, they do provide some insight. Follow up testing is planned to examine the air-void stability of concrete.

1.1. Background

While there has been a large amount of research completed on the bulk properties of air-entrained concrete there has not been a large amount of work done to fundamentally investigate the air-voids themselves or how they change with time. One classic and frequently cited collection on air-entrained concrete is the series of four papers by researchers at the U.S. Bureau of Reclamation [2,4,5,6]. The first [2] of these papers included data suggesting that due to a pressure gradient between large and small bubbles, gas transfer can occur between bubbles. This transfer leads to a change in volume of the air entrained in pastes with time. Photos of air-entrained bubbles in dilute water-to-cementitious materials ratio (w/cm) pastes were also shown to change while sitting statically. Bruere [7] attempted to replicate some of the behavior previously described by Mielenz et al. [2] with a different experimental setup, and found no air bubble instability. In a review of both sets of experiments Powers [8] states that it is doubtful that bubbles will be able to expand in fresh cement paste because of the restraint provided by the cement paste. Other researchers identified a “transition zone” around bubbles that had been frozen during the first 3 h of hydration and observed cryogenically with a low temperature scanning electron microscope (LTSEM) [9–11]. This transition zone was suggested to be filled with water [9] or of a phase with a high porosity [11]. The size of the transition zone was suggested to increase with an increase in w/cm and shrink with hydration. A summary of previous work is provided in Table 1.

2. Experimental methods

To compliment the studies described above, an experimental program was initiated to observe in-situ changes in air bubbles that

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Table 1
Summary of previous research completed on air-void stability and the bubble shell.

Reference and year	Samples	Method of observation	Key observation	Primary conclusion
Meilenz et al. [2]	Paste w/cm 30 AEA/lime/sand/ cement combinations	Stereoscope	Bubbles change size with time and appear to have precipitates on the surface	Pressure differential exists between bubbles
	Paste w/cm 0.3–0.6 prepared in drum mixer	ASTM C 457	Hardened air volume was higher than fresh; discrepancy was larger with higher w/cm	Gas interchange is occurring between bubbles
	Concrete w/cm 0.45 prepared in drum mixer	ASTM C 231	Hardened air volume lower than fresh	
Bruere [7]	Paste 0.45 w/cm prepared with 1000 RPM stirrer set of mixture modified to 5 min, 3, and 8 h	ASTM C 457	No difference in air-void system between samples	No gas interchange between bubbles
Powers [8]	---	---	How can bubbles increase in size if they are confined by paste?	Doubtful if bubbles change size in paste
Rashed and Williamson [9,10]	Mortar w/cm 0.30 concrete 0.29–0.49 w/cm 3 h–3 days w/ and w/o silica fume	Frozen in liquid nitrogen and observed in LTSEM (mortar), SEM (concrete)	Hydration products around air-void appear to be of different morphology from bulk paste; shell observed at 5 min and 3 h; shell made up of fine particles; gap between particles and shells vary in size and appear to contain water during hydration	Shell likely made up of hydration products
Corr et al. [11]	Bubbles isolated by AVA less than 30 min	Frozen in liquid nitrogen and observed in LTSEM	"Mineral" shell seen on individual bubbles and in the paste	Shell observed in individual separation technique similar to one found in paste
	Paste w/cm 0.4 at 5 min		High porosity transition zone "often" observed around bubbles with a 10–15 μm thickness	Transition zone may be increased by freezing

had escaped from cement pastes, and were monitored over time as the bubbles resided in a static bleed-water solution. For this testing, a 0.42 w/cm paste was made using 1.37 kg of a cement meeting the ASTM C 150 specifications for Type I and II with a 0.53 alkali content (Na_2Oeq). Table 2 presents a summary of the admixture combinations investigated. The mixer and mixing procedure used in this study met ASTM C 305. After the mixing cycle was completed, a funnel was used to transfer the paste into a 70 mL bottle that was filled in thirds by volume and consolidated by agitation and taping on the desktop. Care was taken to ensure the bottle did not have any large air-voids and was filled until it reached capacity. At this point the cap was tightened and the bottle was turned on its side. After about 10 min it was possible to observe a layer of bleed water forming at the surface of the paste. In this bleed water air bubbles could be found that had worked their way to the inside face of the bottle wall due to buoyancy. These bubbles were then observed under a stereo microscope at magnification of 500×, fitted with a 5 megapixel, high resolution digital camera. A computer program was written to capture images of the changes in these bubbles with time. These images were measured with the AxioVison AC software from Carl Zeiss. This software allows the user to count pixels between any two designated locations on the image and converts pixels to units of length via an image-specific calibration. Accuracy of the measuring system had been checked and calibrated by the instrument manufacturer. When objects of fixed size were subsequently measured twenty times the software reported coefficients of variation ranging from 0.3% for lengths of 700 μm to 1.3% for lengths of 30 μm. For bubbles sizes reported in this paper a representative coefficient of variation (COV) is about 0.4%, including any effects of distortion by the plastic bottle wall.

Table 2
Mixtures investigated.

Mixture	Admixture	Dosage (mL/100 kg cm)	Setup
1	None	–	1,2
2	Synthetic	47	1,2
3	Tall oil	143	1,2
4	Wood rosin	48	1,2,3
5	Vinsol resin	18	1,2
6	Vinsol resin	26	3
	Water reducer	81	

2.1. Setup #1 — paste expansion

Setup #1 is shown in Fig. 1. In preliminary tests it was found that the paste in the bottle swelled as hydration progressed. Since the bottle was filled to capacity the change in volume of the paste

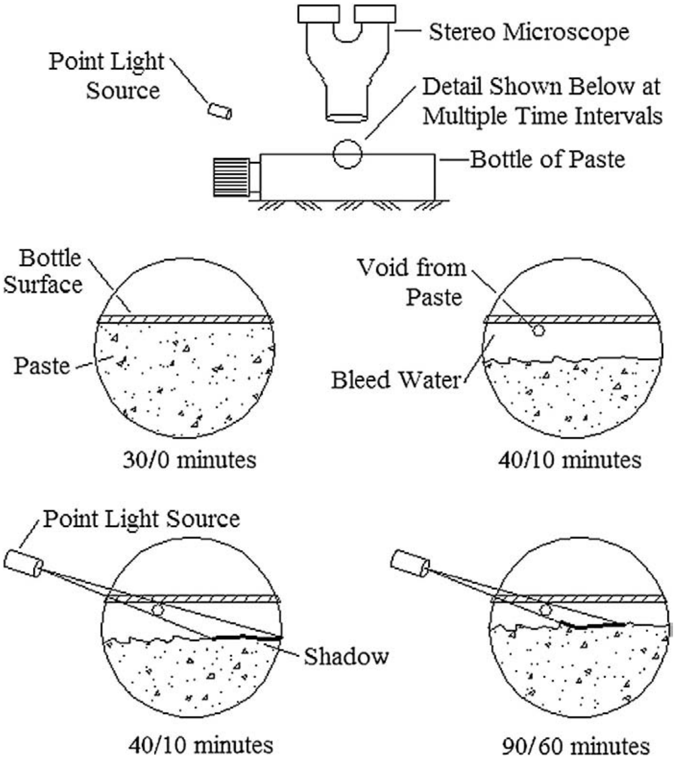


Fig. 1. Setup #1 showing orientation of bottle, stereoscope, and point light source.

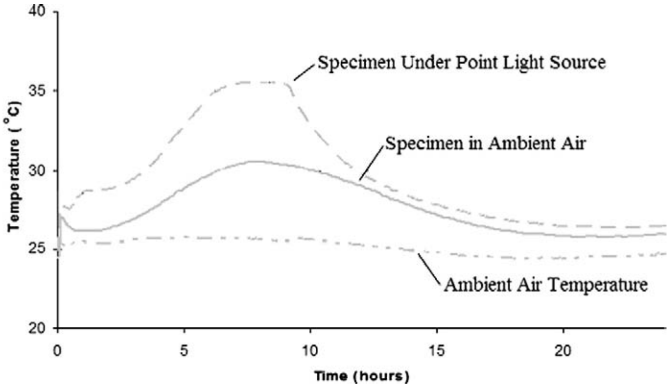


Fig. 2. Time and temperature for the ambient temperature, a specimen under the point light source, and a specimen in the ambient temperature.

disturbed the voids that had escaped the paste and these were then caught on the surface of the bottle in the bleed water. The swelling of the paste was likely related to temperature increase (due in part, perhaps to heat of hydration, and in part to a high-intensity light source), as swelling of the paste was no longer observed once the sample was maintained in isothermal conditions. (A plot of the average temperature from two thermocouples: in the ambient room, in a specimen under the point light source, and in a specimen in the ambient temperature is shown in Fig. 2. These measurements were taken on two different occasions and the results did not vary by more than 1 °C between the measuring periods.) While this swelling was unexpected it proved to be useful as the bubbles could be inspected as they were pushed by the paste from below.

In order to monitor the upwards movement of the paste as it swelled, with respect to the air-bubbles, a single point light source was used at a sharp angle so that the shadow of the bubble could be monitored with time. Since the bubble was stationary at the underside of the bottle wall, an apparent movement of the shadow towards the bubble means that the surface of the paste is moving upwards.

2.2. Setup #2 — no paste expansion

In order to isolate the changes in the bubbles without contact from the paste an alternate setup was used. The only difference in this test setup from the previous is that the bottle of paste was filled to 75% of capacity and the balance of the volume kept full of a surrogate bleed water solution by means of a tube connected to the cap as shown in Fig. 3. The surrogate pore or bleed water solution (w/cm = 60) was carefully added so that it filled the remaining portion of the bottle and the tube, and minimized mixing with the paste in the process. Some agitation was needed to remove air bubbles trapped during filling with the bleed water solution, accomplished by flicking the tube of the bottle with a finger. After this solution was added the bottle was carefully turned on its side and the paste formed a slope as shown in Fig. 3. After 10 min in this position air bubbles were seen to escape from the 0.42 w/cm paste, and floated up to the underside of the bottle. Changes in the bubbles were then observed with time as previously described. Because the bottle was not filled to capacity, once it was put on its side the bleed-water filled gap isolated the bubbles from contact with the expanding paste. This ensured that any changes in bubble diameter with time were solely due to interactions between the bubbles and the surrounding fluid in combination with any effects of temperature-changes in the air within the bubbles.

2.3. Setup #3 — varying fluid pressure

A final setup was used to investigate the effect of pressure on escaped air bubbles from cement paste. While additional work is underway in this area, these test results were included because they indicate that the stability of bubbles may be influenced by changes in the surrounding fluid pressure from concrete placing methods, consolidation, and by the static head of the fresh concrete. Specimens from setup #2 were prepared and the fluid surrounding the air-bubbles was increased to 0.7 bar above atmospheric pressure in 10 equally-spaced steps and then decreased back to atmospheric pressure in three equal steps. It should be noted that the pressure regime was chosen based on limitations of the available equipment.

3. Results and discussion

3.1. Results of setup #1—paste expansion

3.1.1. Air bubbles from air-entrained cement paste

The images of escaped air bubbles from an air-entrained cement paste with a tall oil AEA as per mixture 1 in Table 2 (per setup #1) are shown in Fig. 4. These experiments have been completed 3 times with a tall oil, Vinsol resin, wood rosin, and synthetic AEA at dosages typical of air entrained concrete, and similar behavior was observed for all. A summary of experiments is shown in Table 2. These images were chosen as they are a representative set that clearly shows the behavior. The air-entrained bubbles in Fig. 4 appear to have a textured surface similar to that observed by Mielenz et al. [2] and Corr et al. [11]. Further analysis of these shells and possible mechanisms for their formation is presented in Ley et al. [12]. If one compares Fig. 4a and b the shadow of the air-voids from the point light source has moved towards the bubble with time. The point of focus of the microscope was never changed and the bubbles have remained in focus the entire time; therefore, the depth between the bottle surface and the bubble did not change beyond the depth of focus, which for this instrument at this magnification is about 1 mm. As shown previously in Fig. 1 this is only possible if the paste is expanding towards the bottle surface. Once the paste swells enough to touch the bubble, the shell appears to crack in a brittle manner as shown in Fig. 4c. As the paste swells further one can see a bubble that appears to emerge from the inside of the cracked shell. This is shown in Fig. 4d and e. This emerging bubble seems to have a different, much smoother surface than the shell that was previously observed. As the paste continues to swell and the bubbles are forced to interact no coalescence is observed as the bubbles touch one another (Fig. 4d and e). In Fig. 4e one can see that as bubble B and A come into contact with each other the surface of bubble B appears to have curved away from the surface of bubble A. As further paste expansion occurs in Fig. 4f bubble A appears to have surrounded bubble B without coalescence. In this case, bubble B (with its intact shell) is in a thin film of water on the bottle surface, surrounded by the air from bubble A.

3.1.2. Air bubbles from non-air-entrained cement paste

The images from a non air-entrained cement paste observed in test setup #1 are shown in Fig. 5. The bubbles in this system appear to be translucent-to-transparent and may have some material on the bubble wall but do not have the rough or opaque surface texture

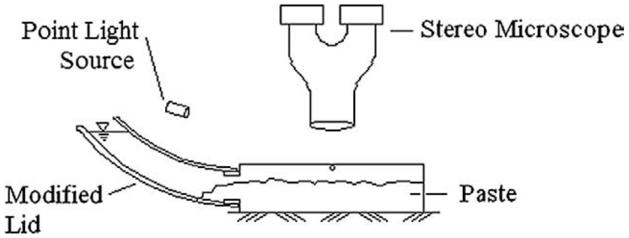
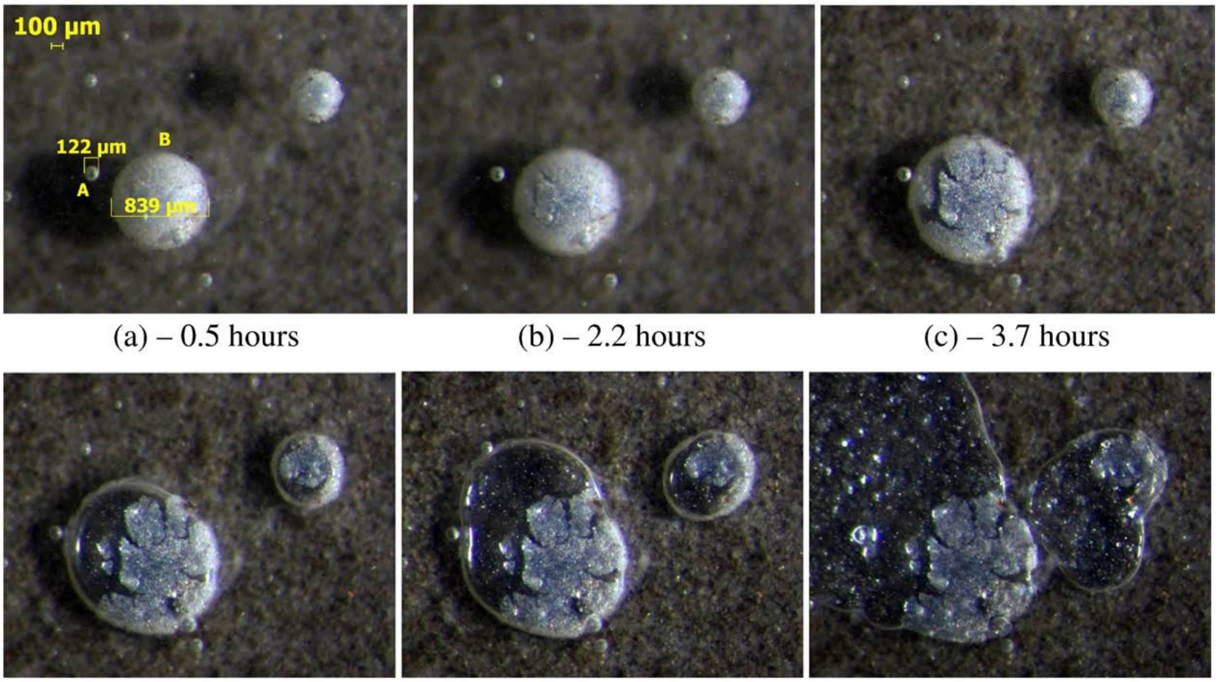


Fig. 3. A cross section of setup #2 showing the reduced paste level and additional water provided by the tube with the modified lid.

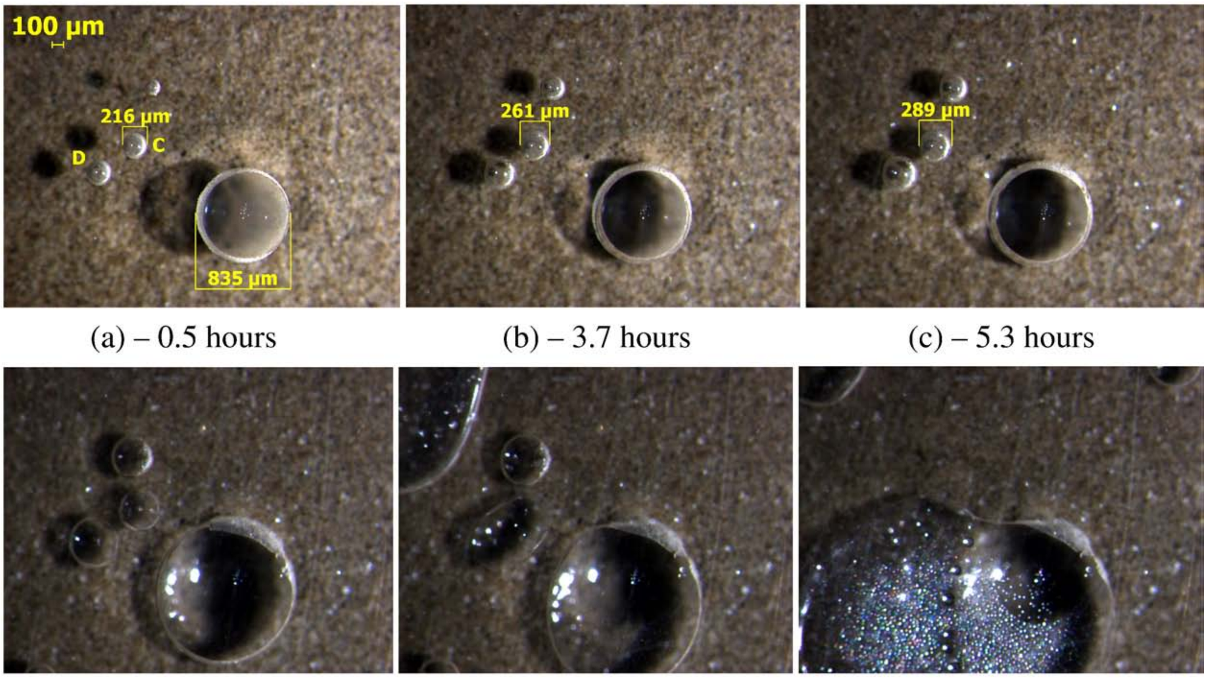


(a) – 0.5 hours (b) – 2.2 hours (c) – 3.7 hours

(d) – 4.8 hours (e) – 5.5 hours (f) – 6.6 hours

Fig. 4. An air-entrained paste (tall oil AEA at 143 mL/100 kg cm) in setup #1 whose bubbles are pushed by the paste below. Please see supplementary data for more information.

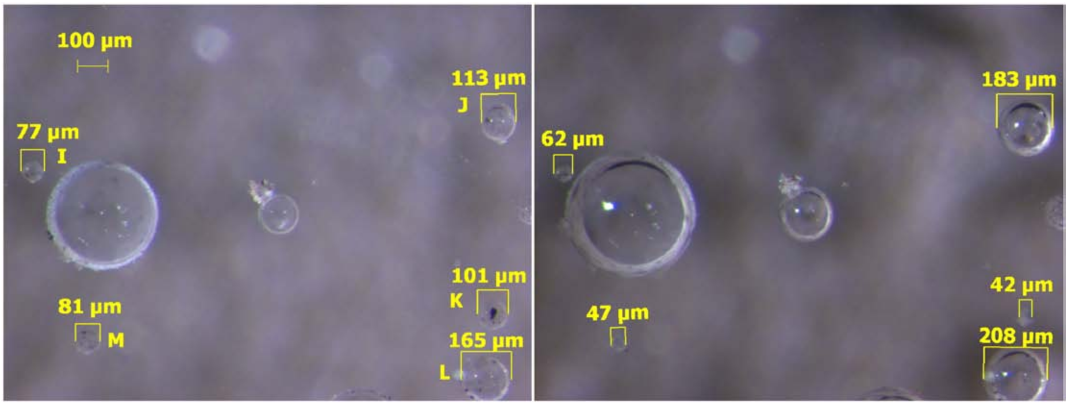
previously observed with bubbles escaped from air-entrained paste. Again the shadows of the bubbles from the point light source move closer to the bubble with time while the bubble is stationary, and so again the paste appears to be rising upwards. Once the paste contacts the bubble, one can see that the bubble diameter begins to expand without an apparent change in the bubble surface. As paste expansion and the accompanying bubble deformation continues, Fig. 5e shows that once bubbles C and D come into contact they coalesce and form a larger bubble. This behavior contrasts with that observed in the previous experiment in which bubbles that escaped from air-entrained paste appeared to resist coalescence. Several dimensions are given for bubble C in Fig. 5a, b, and c showing that this bubble did



(a) – 0.5 hours (b) – 3.7 hours (c) – 5.3 hours

(d) – 6.8 hours (e) – 7.3 hours (f) – 7.8 hours

Fig. 5. A non-air-entrained paste sample in setup #1 whose bubbles are pushed by the paste below. Please see supplementary data for more information.



(a) – 0.5 hours (b) – 3.6 hours

Fig. 6. A non-air-entrained paste sample in setup #2. 6a is taken 0.5 h and 6b is taken 3.6 h after hydration began. Please see supplementary data for more information.

change diameter with time before it came into contact with the expanding paste (as indicated by the shadow technique described earlier.) This is discussed further in Setup #2. This test was repeated three times with similar behavior each time.

3.2. Results of setup #2—no paste expansion

3.2.1. Bubbles from air-entrained cement paste

When air-entrained cement paste was tested in this setup, there was no measurable change in the diameters of the bubbles that had escaped into the fluid above the paste over the 8-hour period of observation. This test was repeated four times with a similar size distribution of observed bubbles and little to no diameter change was observed for the following AEAs investigated: tall oil, Vinsol resin, wood rosin, or so-called “synthetic” as reported in Table 2.

3.2.2. Bubbles from non air-entrained cement paste

When bubbles from non air-entrained cement paste were examined over time in setup #2, it was found that there was a significant change in bubble diameter for the first 3.5 h after hydration. A picture of the layout of the bubbles is shown in Fig. 6 at 0.5 and 3.6 h of hydration, and the same translucent-to-transparent bubble walls are evident as seen earlier when the bubbles originated in non air-entrained paste. A graph summarizing the average change in diameter with time is shown in Fig. 7. For the diameters reported in Fig. 7, two measurements were taken that were perpendicular to one another and then averaged. As can be seen bubble “I” begins to decrease in size from the initial observation until about 1 h of hydration. Bubbles “M” and “K” begin to decrease in size at about 2 h after initial hydration and stabilize after about 3 h. Bubbles “J” and “L” begin to increase in size from the initial observation and stabilize at 2 h of hydration. The smaller bubbles appear to decrease in size initially while the larger bubbles appear to increase in size. The mid-sized bubbles remain a constant diameter initially, and then start to decrease in size. A proposed explanation for the size change of different diameter voids has been suggested by Fagerlund [3], who hypothesized that the smallest (higher-pressure) bubbles lose air to the largest (lower pressure) bubbles while intermediate sized bubbles would show no volume change. Thus all bubbles in the system tend towards an equilibrium pressure and size. Fagerlund went on to propose that the bubble-size distribution would continuously change until such an equilibrium is reached. The observations of this present experiment not only support Fagerlund's ideas, but are also similar to the observations by Mielenz et al. [2] for air-entrained paste with a w/cm of 30. The experiments reported here were repeated 4 times and each time many, but not all, of the smaller bubbles decreased in size over time while the larger bubbles increased in size.

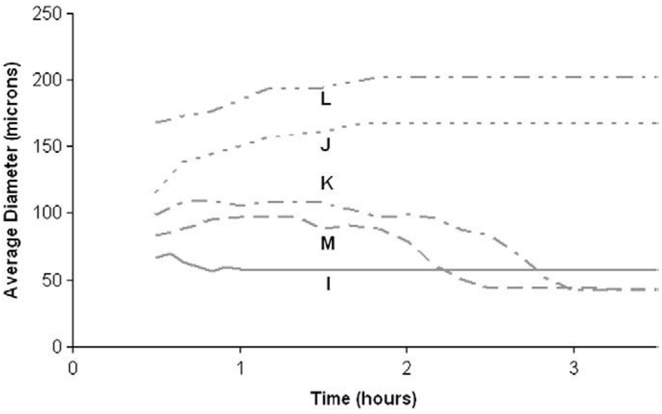
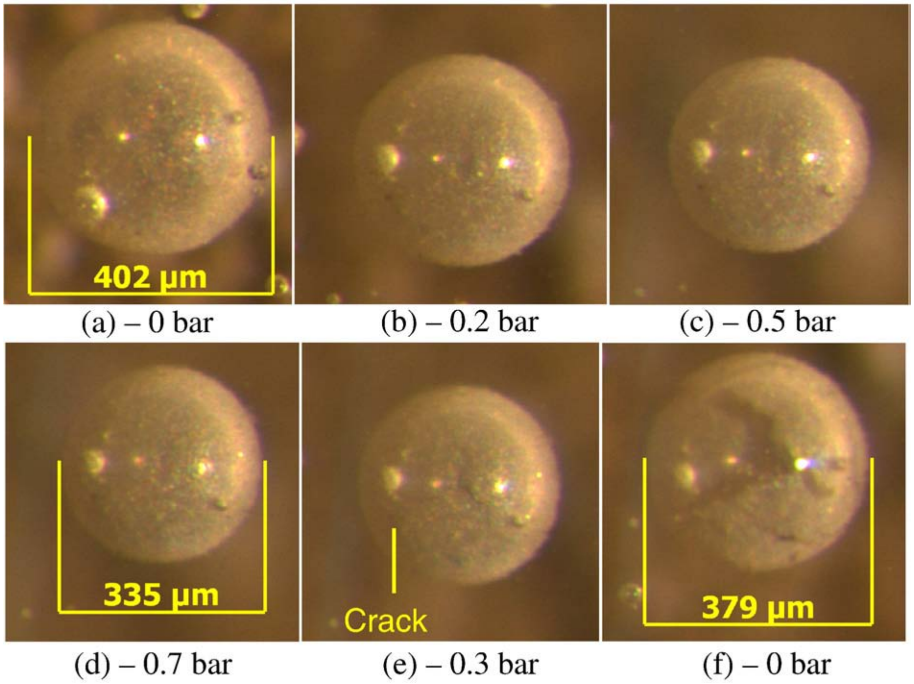


Fig. 7. Average diameter of bubbles in a non-air-entrained paste specimen as shown in Fig. 6 in setup #2.

3.3. Setup #3—varying fluid pressure

3.3.1. Response of air bubbles to pressure

In Fig. 8a an approximately 400 µm diameter bubble from mixture 6 is shown at atmospheric pressure. One first notices that the bubble shell with the Vinsol Resin and water reducer used here appears to be different from the shell observed in Fig. 4, which had been stabilized with a tall oil AEA and no water reducer. There appears to be a difference in color of the shells and the particle size that makes up the shell surface. This difference is likely important, and further discussion of the difference in behavior between shells created with different admixtures is discussed further in Ley et al. [12]. Further, in Fig. 8a through d the fluid pressure around the bubble is being increased. In Fig. 8d one can see that the air bubble has decreased in diameter such that bubble volume at 0.7 bar overpressure is 58% of the volume of the same bubble at 0 bar overpressure. Since simple application of Boyle's Law would have predicted 59%, it appears that this particular bubble is behaving as an elastic, gas-filled body with no significant surface tension effects. (The degree to which this finding can be generalized to other bubble sizes, stabilized with other AEA's deserves further investigation, some of which is already in progress.) Further, it is interesting to note that the shell around the bubble does not appear to be distressed by the significant decrease in diameter during the pressurization phase; however, observations with a higher magnification may yield other observations. In Fig. 8e and f the fluid

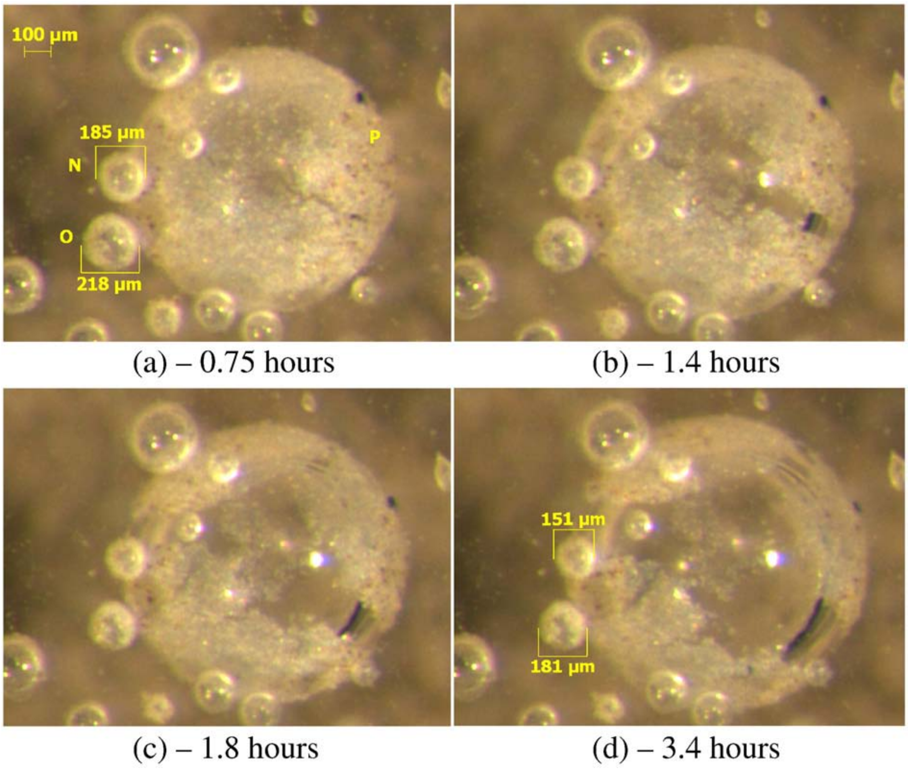


(a) – 0 bar (b) – 0.2 bar (c) – 0.5 bar

(d) – 0.7 bar (e) – 0.3 bar (f) – 0 bar

Fig. 8. The response of bubbles escaped from a mixture containing 26 mL/100 kg cm of Vinsol resin and 81 mL/100 kg cm of normal WR subjected to a pressure 0.7 bar above atmospheric and then returned back to atmospheric pressure.

pressure is reduced to atmospheric pressure. As this is taking place one can see in Fig. 8e that the shell of the large air bubble cracks as the bubble is increasing in volume during the depressurization phase. These cracks widen in Fig. 8f as the fluid returns to atmospheric pressure. It can be seen that the void is no longer covered by the shell. Furthermore, it appears that some air contained in the bubble has been lost to the surrounding fluid during the overall pressure cycle as the final diameter does not match the initial diameter (net reduction in diameter of 6%, which would correspond to about a 17% reduction in air volume if the internal pressure was the same before and after the pressure cycle was applied). This experiment has been repeated over 10 times with Vinsol resin and wood rosin AEAs at dosages shown



(a) – 0.75 hours (b) – 1.4 hours

(c) – 1.8 hours (d) – 3.4 hours

Fig. 9. An air-entrained paste sample with wood rosin AEA at 48 mL/100 kg cm in setup #3. Please see supplementary data for more information.

in Table 2 and each time many but not all bubbles with diameter of 200 µm or greater were observed to crack while the pressure was decreased. (These images were chosen for their clarity.) From observations at this magnification it is difficult to observe if the shells of smaller bubbles are also damaged upon depressurization.

3.3.2. Changes in a bubble with time after the shell has been damaged

Pictures in Fig. 9 show the changes in a collection of bubbles stabilized with a wood rosin AEA from mixture 4 over approximately three hours after being subjected to a pressure of 0.7 bar and returned to atmospheric pressure. The pictures in Fig. 9 show the changes in the collection of bubbles at the conclusion of pressure cycle. As can be seen the shell of the bubble labeled P in Fig. 9 has been damaged during the depressurization phase and appears to be "shed" by the bubble over time. Also the smaller bubbles N and O surrounding the large bubble P appear to shrink in diameter as P appears to expand. It should be noted that several other bubbles very close to bubble P do not show a change in size. It is unclear why only bubble N and O decreased in size. Perhaps only the shells of these bubbles were damaged during the change in pressure or perhaps as Fagerlund [3] suggested, bubbles of this intermediate size are not yet affected by the pressure differential. Furthermore, voids N and O decreased to a certain size and then stabilized. This is the same general behavior observed in the non air-entrained paste shown in setup #2 and had been observed by Mielenz et al. [2]. While cracking of air-bubble shells was observed many times in this present experimental series due to an increase and decrease in the surrounding fluid pressure, there are insufficient observations to allow one to make general statements over how a system of bubbles will respond.

As an interesting potential consequence of the observation of changes in bubble size, consider that the air bubbles observed here in water-suspension may be similar to those in cement paste that are surrounded in-place by a water filled "gap," as observed by others [9–11]. It would then seem plausible that gas permeability of the bubble shell would influence gas interchange among bubbles of various sizes and internal pressures as also proposed by Mielenz [2] and Fagerlund [3]. This interchange could lead to a decrease in volume of the smaller bubbles and an increase in volume of the larger bubbles as observed in the experimental work in this paper. This change in void volume could ultimately lead to a higher overall air content in a concrete mixture as first suggested by Mielenz et al. [2]. This phenomenon could be an explanation for observations of increased air contents (i.e., higher air contents measured in hardened concrete as compared to air contents measured in fresh concrete using a pressure meter [13] as reported in field concrete [14] and in past research [2,15].

4. Summary of key observations

In this paper, some background is presented on the changes in a static air-void system in concrete and paste. Results from three different setups are presented that may provide insight into the fundamental behavior of air bubbles in water that have escaped from air-entrained and non air-entrained pastes. The degree to which these observations pertain to actual air bubbles fully surrounded by cement paste remains to be determined. It is pointed out, however, that the air void analyzer [16], considered by proponents of the method to give representative air bubble distributions, liberates air bubbles into a water–glycerine solution in a far more energetic manner than was done in these experiments.

1. An opaque "shell" was observed on the exterior of air bubbles that had escaped from air entrained paste. The appearance of the shell changed as different AEA admixtures were used.
2. In these experiments with bubbles in bleed water, bubbles with an opaque shell appeared to resist coalescence, whereas translucent-to-transparent bubbles coalesced readily. Similarly, the shell appeared to take on structural properties such as stiffness, resistance to deformation, and eventual cracking. The role of these properties in stabilizing air bubbles within cement paste has not been identified.
3. When the shell appeared to be fully intact over observable portions of the bubble surface, the diameter of the bubbles did not change with time for the conditions of setup #2. When a readily discernable shell was not present as in the specimen of non air-entrained paste in setup #2, the diameter of the air bubbles was observed to change with time. Likewise, of those bubbles with a readily observed shell, only those that had cracked changed diameter with time.
4. In pressurized experiments shown in setup #3 it was observed that the air-bubble shell was damaged during depressurization from 0.7 bar to atmospheric pressure. This may be important in construction applications in which the concrete pressure is increased and decreased. It is not known, however, whether the experimental observations made here under a relatively mild and slow pressure change apply equally to the much higher pressure differences and rates of pressure change experienced in concrete pumping, for example.
5. A single shell-covered bubble that had escaped from air-entrained paste was observed to decrease in volume under pressure precisely as would be predicted by Boyle's Law, with no apparent influence of the shell.

The observations reported here have been of air bubbles suspended in surrogate bleed water above paste. These observations may or may not be valid in concrete, and more research is clearly needed in this interesting and critical area of the stability of air bubbles in fresh concrete. Nevertheless the role played by what appears to be a shell of sorts at the periphery of air bubbles in air entrained concrete deserves attention.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cemconres.2009.01.019.

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