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INFLUENCE OF LOW ATMOSPHERIC PRESSURE ON FLUIDITY AND PORE SIZE OF CEMENT PASTE

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Air entraining admixture is often used to improve fluidity and freeze-thaw resistance of concrete through introducing dispersed micro bubbles. Driven by the Great Western Development Strategy and the Belt and Road Initiative of China, a large amount of concrete are used for the construction at high altitude areas of western China. But it was found that the fluidity and freeze-thaw resistance of concrete decreased a lot due to low atmospheric pressure at high altitude. To explore the influence of low atmospheric pressure on the performance of cementitious material, flow-through time of cement paste and pore size of hardened cement paste were tested. The flow-through time at 20 kPa was increased by 27.6% to 135.0% compared to normal atmospheric pressure (100 kPa). As the atmospheric pressure decreased from 100 kPa to 40 kPa, the average pore diameter of the high W/C hardened cement paste decreased to 75.3% to 71.3%, whereas the average pore size of the low W/C hardened cement paste increased by 39.0%. This reflects that the fluidity and the freeze-thaw resistance of cementitious material will decrease more or less at lower atmospheric pressure. The changes of fluidity and freeze-thaw resistance durability may be explained by the increased diameter of bubbles in fresh cement paste at lower pressure.

Keywords: *Low atmospheric pressure; Pore; Bubble; Air entraining admixture*

1. Introduction

Concrete is the most widely used building material in the modern world [1]. There are many plateaux and mountains in western China, which hinders the social and economic development of this region. The Chinese government introduces some national development strategies such as *the Great Western Development Strategy* and *the Belt and Road Initiative* to promote the development of western China. Driven by those strategies, a large volume of concrete is manufactured for the construction at high altitude areas. In 2016, the output of premixed concrete was 2.23 billion m^3 in China, of which 0.5 billion m^3 were produced in western region, accounting for 22% of the total output. Even more the year-on-year growth rate of concrete construction over there is the highest, for example, the average growth rate in Tibet reached 14.29% in recent year.

During the manufacture of concrete, air entraining admixture is added to make separated small bubbles in the concrete to increase the fluidity of the concrete and in the meanwhile enhance the freeze-thaw resistance of the concrete [2]. However, as the altitude increases, atmospheric pressure gradually decreases (Figure 1). It has been found that the concrete air content decreases which leads to the fluidity and freeze-thaw resistance decreases in the low-pressure environment of high plateau. It was found that when the atmospheric pressure reduced to 50 kPa, the air content of concrete decreased by about 20%~49% and the bubble spacing factor increased to 200~300 μm [3]. At higher altitude the atmospheric pressure is lower, and introducing micro air bubbles is hard to achieve. Conversely, unwanted big air bubbles are introduced which will affect the strength and freeze-thaw resistance of the concrete.

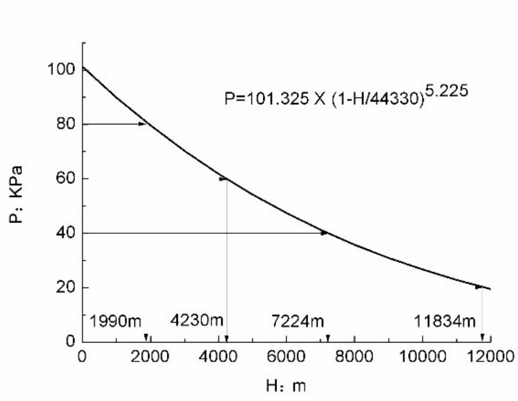

Fig. 1 - Relation curve of pressure and altitude.

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Li *et al*. believed that low atmospheric pressure increased the surface tension of the air entraining admixture, resulting in a reduction in the effectiveness of the air entraining admixture [3]. However, the research of aqueous film forming foam extinguishing agent (a surfactant) found that the surface tension of surfactant changed no less than 1 mN / m from 520 m (atmospheric pressure 94.6 kPa) to 4300 m (atmospheric pressure 61.0 kPa) [4]. Low atmospheric pressure had little effect on the surface tension. The change of surface tension may not be the main reason. The reason for the decrease of fluidity and the increase of spacing factor in concrete at high altitude is not clear by now.

The air bubbles in concrete have direct relationships with the fluidity and pore of concrete. There are some direct methods for the observation of bubbles in fresh concrete, such as optical fiber test [5], 1H low-field NMR test [6], CT technology test [7], AVA air void analysis [8,9], cryogenic freezing test [10], and stereomicroscope observation [11,12]. Bubbles measured by these test methods are in the fresh concrete mixed at normal atmospheric pressure（100 kPa）. For simulation studies on the performance of fresh concrete manufactured in the plateau, it is needed to form the mixing process and the bubble observation process in a sealed system, and keep the system always at a constant low atmospheric pressure corresponding to the altitude. So far, no one has tried this.

In this paper, new test devices were designed to prepare cement paste and test performance of cement paste in a sealed system. The fluidity, pore and air bubbles were tested at designed low atmospheric pressure in this system. The results contribute to the understanding of the influence of low atmospheric pressure on the fluidity and pore of cementitious material.

2.Materials and experiments

2.1.Materials

P.I 42.5 cement was used in the experiment. The chemical composition and physical properties are shown in Table 1 and 2.

Air entraining admixture (AEA) was a light yellow Saponin powder. 0.1% AEA aqueous solution was prepared for the experiment.

2.2.Experimental equipment and test methods

Flow-through time of cement paste, pore of hardened cement paste and bubble diameter in cement paste were tested at low atmospheric pressure.

(1) Flow-through time of cement paste

Flow-through time tester of cement paste was shown in Figure 2. Tester and vacuum pump were connected through a rubber gas tube. The outer diameter of the rubber gas tube was 14 mm and inner diameter was 8 mm. The constant pressure separating funnel was divided into two parts by a piston. The upper part and the lower part were connected by a glass tube to make sure the pressure of the tester were same, so that the liquid flowed down freely. The single-neck flask was used to hold cement paste that flows down from the funnel.

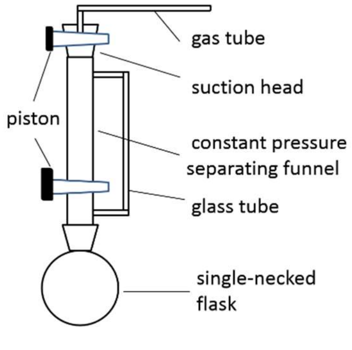

Fig. 2 - Schematic diagram of flow-through time tester.

Raw materials were added into the funnel. The tester was evacuated to the designed test pressure quickly (approx. 20 s) through the gas tube by a vacuum pump. Then, closed the piston of suction head. Turned the tester upside down 180 ° and shook up and down 100 times quickly to make the cement paste mix well.

After that, opened the piston of the constant pressure separating funnel to allow cement paste flowed freely into the single-necked flask. The

Table 1

P.I 42.5 cement chemical composition (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	f-CaO	Loss
22.87	4.47	3.48	64.05	2.46	2.44	0.52	0.90	1.21

Table 2

P.I 42.5 cement physical properties

Fineness (%)	Density(g/cm^3)	Specific surface area（m^2/kg）	Standard consistency water demand（%）	Soundness（mm）	Setting time（min）		Flexural strength（MPa）		Compressive strength（MPa）	
					Initial	Final	3d	28d	3d	28d
0.8	3.15	345	25.8	4	142	202	6.0	9.3	27.2	48.7

flow-through time (from opening piston till cement paste flowing finish) was recorded by stopwatch.

(2) Pore size of hardened cement paste

Cement specimen-making device was shown in Figure 3. The barometer continuously monitored the pressure inside. The sealing cover was used to maintain air pressure stability. A plastic bottle was used to mix the raw material and mold the cement paste specimen. The plastic bottle is a rectangular parallelepiped, the bottom side length 40 mm * 40 mm, height 100 mm.

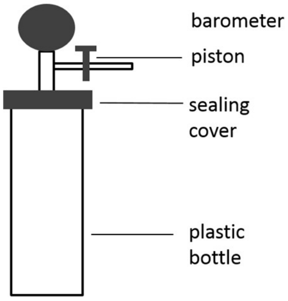

Fig. 3 - Schematic diagram of specimen-making device.

Raw materials were added to the plastic bottle firstly, sealed the plastic bottle by the cover. Then, evacuated pressure in the plastic bottle to the designed pressure. After that, closed the piston, vibrated the plastic bottle up and down 100 times quickly to mix the cement paste well.

After cured at 20℃ for 24 h (Low pressure has little effect on the pore structure of the hardened cement paste), cut the plastic bottle and removed the cement paste specimen from the plastic bottle.

Then, the cement paste were cut parallel to the bottom, then ground and polished the new surface cut out. Photographed specimen by a stereo microscope (Motic SMZ-168). Microscope photo were analyzed using Image-Pro plus 6.0 software. Chosen a 400 pixels * 400 pixels AOI (area of interest)，Analyzed the size and number of pore in this AOI. Due to severe deformation of the plastic bottle at 20 kPa pressure, the paste specimen was difficult to mold. The hardened pore structure test of the cement paste was done at 100kPa, 80kPa, 60kPa, 40kPa.

(3) Air bubble in fresh cement paste

To observe the diameter of bubble in fresh cement paste, the in situ bubble observation system was designed as shown in Figure 4. The maximum magnification of the stereo microscope（Motic SMZ-168）was 200 times. The acrylic bubble observation room (Figure 5) was all transparent so that the bubble in the cement paste can be observed by Motic SMZ-168 from outside. There was a piston on each side of the observation room. When the two pistons were closed, the observation room kept the pressure alone. The two-necked glass flask was used to mix the raw material to make cement paste. The observation room and the two-necked glass flask were connected by a connecting catheter. The outer diameter of rubber connecting catheter was 14 mm and inner diameter was 8 mm, so as to ensure that the liquid in the tube could flow freely at low atmospheric pressure. The connecting catheter could be removed after the paste was transferred to the observation room.

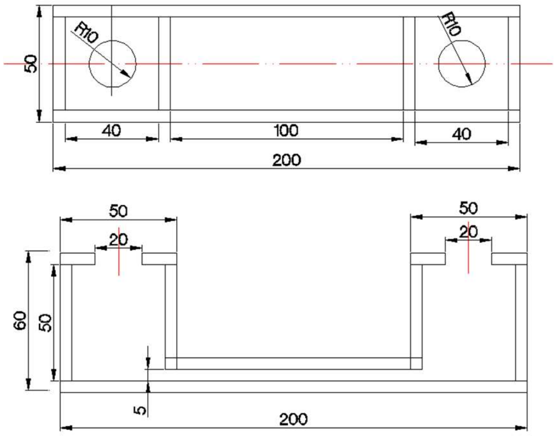

Fig. 5 - Drawings of bubble observation room.

The preparation of cement paste and the observation of the bubble were carried out at the designed pressure. Firstly, raw materials were added into the two-necked flask. Then, connected the vacuum pump and evacuated the pressure in the system to the designed pressure quickly (about 30s). After that, shook the flask up and down 60 times to mix the cement paste evenly. Finally, transferred the cement paste from the two-necked flask to the bubble observation room through the connecting catheter by gravity, closed the piston of the observation room, and removed the connecting

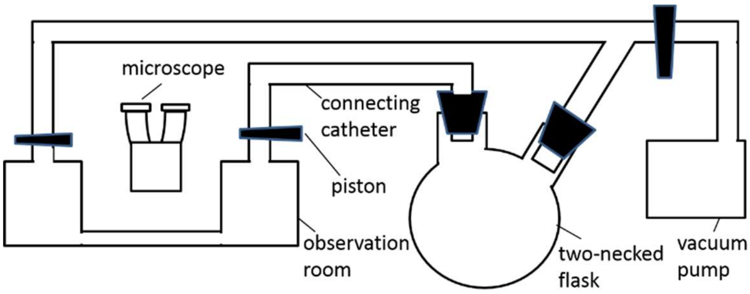

Fig. 4 - Bubble in situ observation system.

Table 3

The mix proportion of cement paste

Test items	Group	Water (g)	AEA aqueous solution (g)	Cement (g)
flow-through time test	Group A	50	0	100
	Group B	40	10	100
Pore test	Group A	15	0	30
	Group B	12	3	30
	Group C	7.5	3	30
Bubble test	Group A	30	0	60
	Group B	24	6	60

catheter, Put the bubble observation room under the microscope to observe.

Photographed the bubbles in the observation room. The time from adding water to getting the photos was about 5mins. Microscope photos were analyzed using Image-Pro plus 6.0 software. Due to the small difference between the gray value of the bubble and the cement paste, all the visible bubbles in the photo were manually selected for measurement.

2.3.Experimental design

In the experiment three groups of cement paste A, B, C were designed. Group A was the reference group (only water and cement). Group B and C were test groups with 0.01% AEA. The W/C in group A, B and C was 0.5, 0.5 and 0.35 respectively. Five atmospheric pressures (100kPa, 80kPa, 60kPa, 40kPa, 20kPa) were designed for each group. The AEA aqueous solution dosage for all groups was 10 wt% of cement. The mix proportions of cement paste are shown in Table 3.

3.Results

3.1.Fluidity of cement paste

Flow-through time test was used to test the fluidity of cement paste. The longer flow-through time, the lower is the fluidity. The results are shown in Figure 6.

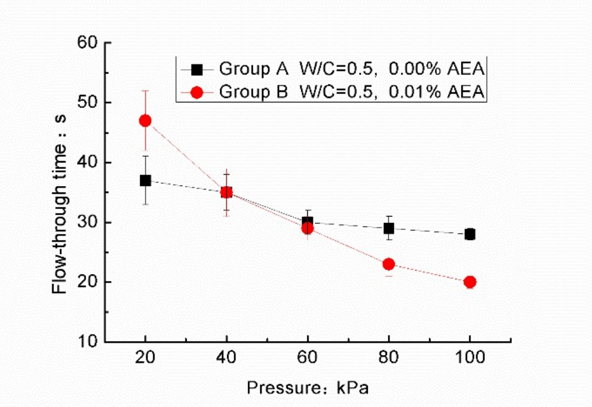

Fig. 6 - Cement paste flow-through time at different pressure.

Compared the fluidity of Groups A and B at normal atmospheric pressure(100kPa), it can be found that the flow-through time decreased from 28 s to 20 s after AEA was used. AEA increased the fluidity of cement paste at normal atmospheric pressure.

In addition, when atmospheric pressure reduced from 100 kPa to 20 kPa, flow-through time of Group A increased from 28 s to 37 s, increased by 27.6%. The fluidity of the Group B decreased more. As atmospheric pressure from 100 kPa downed to 20 kPa, cement paste flow-through time increased from 20 s to 47 s, increased by 135.0%. With the atmospheric pressure decreased, the flow-through time of cement paste increased.

3.2.Pore of hardened cement paste

The photos of Group A, B and C at different.

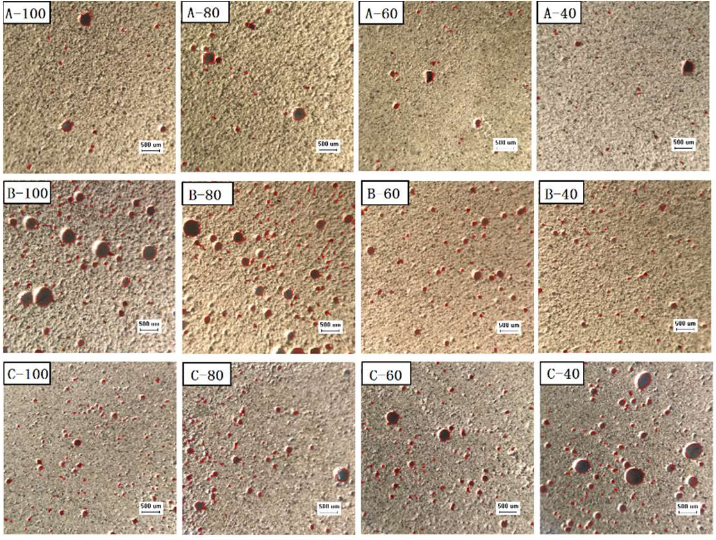

Fig. 7 - Pore of hardened cement paste at different pressures (× 30).

Table 4

Pore diameter test results of hardened cement paste

Sample	Atmospheric pressure (kPa)	Average pore diameter (μm)	Pore number	Rate to reference (100 kPa) (%)
A-100	100	93.7	21	100
A-80	80	93.4	30	99.7
A-60	60	80.5	25	85.9
A-40	40	70.6	26	75.3
B-100	100	91.4	102	100
B-80	80	87.9	119	96.2
B-60	60	84.7	62	92.7
B-40	40	65.2	60	71.3
C-100	100	65.7	81	100
C-80	80	77.6	85	118.1
C-60	60	79.1	89	120.4
C-40	40	91.3	110	139.0

pressure were shown in Figure 7.

The analysis results using Image-Pro plus 6.0 were shown in Table 4.

By comparing A-100 and B-100with the same W/C=0.5, it was found that the number of pore increased from 21 to 97. The addition of AEA significantly increased the pore number in cement paste. As the atmospheric pressure decreased from 100 kPa to 40 kPa, the average pore size of the hardened cement paste in Group A and B. decreased to 75.3% and 71.3% respectively.

However, diameter changes of hardened cement paste in Group C were different from those in Group A and B. As the atmospheric pressure decreased from 100 kPa to 40 kPa, the average pore diameter increased from 65.7 μm to 91.3 μm, increased 39.0%.This result is consistent with the result of Dils’ experiment in which prepared cement paste in vacuum and tested pore diameter of the hardened cement paste at atmospheric pressure [13].

4.Discussion and analysis

The bubbles in fresh cement paste are directly influence the flow-through time and the pore diameter of the cement paste. Studying the bubbles changes in the paste at different pressures may explain the influence of the low pressure on the fluidity and frost resistance durability. Bubble in fresh cement paste of Group A and B at different pressures are shown in Figure 8.

In Figure 8 and 9, when the atmospheric pressure decrease from 100 kPa to 20 kPa, the average diameter of bubble in Group A and B increased by 95.8% and 79.6%. For Group A, the average diameter increase from 95 μm to 186 μm; For Group B, the average diameter increase from 60 μm to 110 μm.

The increases of bubble at low atmospheric pressure lead to the changes of fluidity in the fresh paste and the pore diameter of hardened cement paste.

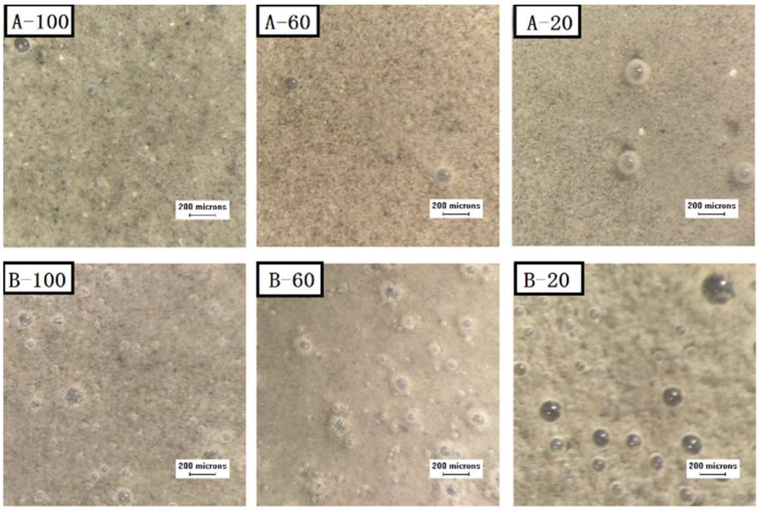

Fig. 8 - Photos of bubbles in air-entraining fresh cement paste at different pressure (× 80).

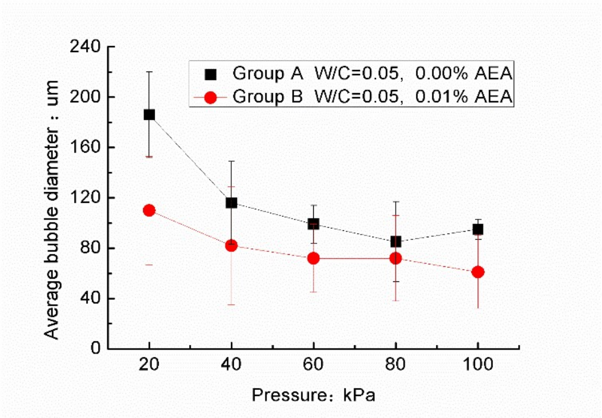

Fig. 9 - The average diameter of the bubble in fresh cement paste.

(1) Fluidity of cement paste

Air-entraining agent can increase the fluidity of the cement paste and the flow-through time of the paste decreases at normal atmospheric pressure (100kPa). This is mainly because the AEA is surfactant that disperses the cement particles, and the “ball bearing action” increase, thereby increase the fluidity of the cement paste [14].

Comparing with normal atmospheric pressure (100 kPa), the fluidity of the paste decreased at low atmospheric pressure (80 ~ 20 kPa). That is mainly due to the increased bubble diameter in the low atmospheric pressure paste, which increases the resistance of the paste through the constant pressure funnel. In addition, the “ball bearing action” may decrease due to the change of bubble diameter. So the flow-through time increases and the fluidity decreases at low atmospheric pressure.

(2) Pore of hardened cement paste

In Group A and B (W/C=0.5), the pore diameter of hardened cement paste decreases with the decrease of air pressure, while the pore diameter of hardened cement paste increases with the decrease of air pressure in Group C (W/C=0.35). The pore of the hardened cement paste can be explained by the Stokes formula [15]:

$$V_p = \frac{1}{18}\frac{\rho_l-\rho_g}{\mu} \times g{d_p}^2 \text{..........} \quad (1)$$

The density of air ρ_g is 1.295×10^{-3} g/cm^3 at normal atmospheric pressure. The density of cement paste ρ_l of Group A, B and C is 1.429 g/cm^3, 1.429 g/cm^3 and 2.132 g/cm^3 respectively. The density of air at lower pressures is smaller than at normal atmospheric pressure. The density of cement paste is at least 1000 times the air density. So (ρ_l - ρ_g) can be approximately equal to ρ_l. The viscosity μ of Group A, B and C cement paste at 5 min is 60.2 mPa·s, 40.8 mPa·s and 1147.0 mPa·s respectively. Assuming that the diameter of the bubbles in the paste is 100 μm.

The parameters of the three groups A, B, and C are brought into the formula, and the bubble rising speeds are respectively determined to be 47.5 mm/h, 70.0 mm/h, and 3.7 mm/h respectively. (The height of hardened cement paste specimen is about 15 mm). In the actual process, with the hydration process of the cement paste, the viscosity of the slurry increases. The actual rise rate is smaller than the calculated value.

At low atmospheric pressure, the diameter d_p of the bubble generated in the cement paste increases which brings the increases of V_p. So the bubble rises faster than at normal atmospheric pressure. Therefore, during the preparation of the cement paste specimen (Group A, B), the bubbles are more likely escape from the cement paste. That results in a smaller pore size of the hardened cement paste at low atmospheric pressures. While the viscosity μ of the cement paste is higher and ρ_l / μ is smaller in Group C. That reduces the velocity V_p of bubble rise. The air bubbles are seem to be solidified in the paste. That leads to a larger pore size in the hardened cement paste finally.

If diameter of pore in concrete becomes larger, the freezing point of the pore solution of concrete increases. The water in the concrete pore tends to freeze easily, and then freeze-thaw resistance of concrete is reduced [16]. Studies have shown that there is a positive correlation between the bubble spacing coefficient of hardened concrete and the average diameter of bubbles [17]. Large bubbles often lead to large bubble spacing factor, reducing the freeze-thaw durability of concrete.

5.Conclusion

Comparing the flow-through time, pore and air bubble of cement paste at normal atmospheric pressure and low atmospheric pressure, the following conclusions were drawn:

1. When the atmospheric pressure decreased, the fluidity of cement paste decreased and the fluidity of cement paste with AEA reduced more than without AEA.

2. As the atmospheric pressure dropped, the pore diameter of hardened cement paste increased in low W/C (W/C=0.35) specimen and decreased in high W/C (W/C=0.5) specimen.

3 The bubble diameter in fresh cement paste increased with the reduction of atmospheric pressure. The increase induced the decrease of fluidity in fresh cement paste and changes of pore diameter in hardened cement paste.

Composition and structure of concrete are more complex than those of cement paste. The influence of low atmospheric pressure on the properties of concrete needs to be studied further. The results obtained in this paper can be used to explain this influence partially. Significant follow-up work to this study has been performed or is in progress, and the findings from these studies, including bubble generation mechanism at low atmospheric pressure, will be reported in future publications.

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