Effect of Air Entraining Agents on The Air Void Structure of Concrete

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Abstract. Four different air entraining agents are selected. The air entraining effect and their foaming stabilities in cement pore solution; the impact on air entrainment in fresh concrete; and the variations in air voids and their structures in hardened concrete are compared and studied. The results show that the development in porosity of the hardened concrete mixed with different air entraining agents is consistent with the air entrainment in fresh concrete; and the variations in air voids and their structures in hardened concrete are compared and studied.

Carboxylic based air entraining agents generate calcium soap, whereby such moiety can effectively encapsulate air bubbles. While the stability is insignificant in cement pore solution, the impact is obvious in concrete. When employed alone, the air entraining agent failed to improve both air entrainment of fresh concrete and final concrete structure. Instead, a combination of air entraining agents is found to induce a synergistic effect, effectively enabling both the air-entraining performance and the development of an enhanced porous structure of the hardened concrete.

1. Introduction

Air entraining agents (AEA) can reduce the surface tension of fresh concrete to ideally generate uniform, stable and optimally packed micro bubbles during the mixing of concrete, improving the workability, frost resistance, carbonization resistance and other durability parameters[1,2]. As a result, AEAs are widely specified and used in concrete field since it first discovered in the mid-1930s[3,4]. Structure and stability of air bubbles depend on the types of AEA. Şahin et al.[5] pointed out that fatty alcohol type AEAs produced small air bubbles, while synthetic and resin type form coarser and mid-sized bubbles. Barfield et al.[6] concluded that different AEAs formed concrete with different air void characteristics, whereby synthetic AEAs produced excellent air-void system. Łaz´niewska-Piekarczyk[7] reported that synthetic AEAs generated the closely spaced and small air voids, followed by AEA made of saponified resin.

Good air void structure distribution are crucial for determining the concrete property[8,9]. Puthipad et. al.[9,10] claimed that fine air bubbles (<0.2 mm) enhance the workability of fresh concrete and improve the frost resistance and final strength of the hardened concrete. On the other hand, large air bubbles are unstable and can escape easily from the concrete, thus reducing the stability and eventual frost resistance of the concrete. Powers[11] reported that the frost resistance of concrete highly depends on the air void size and distribution. Many researchers believe that the frost resistance of concrete, besides mechanical strength, mainly depends on the spacing factor and volume of air content[5,12].
Christodoulou[13] reported that by incorporating AEA, tiny air bubbles form, imparting a ball-bearing effect in fresh concrete that enhances easiness for aggregates movement. Bruere[14] found that the floatation energy of air bubbles reduces the settlement rate of cement particles and decreases bleeding and segregation. Zhang et. al.[15] observed that small air bubbles (10–600 mm) reduced yield stress and viscosity of mortar, whereby the characteristics of the air bubbles have a greater influence on the rheology than that from the total air content. Despite the distinct correlation, AEA are usually evaluated by the air content of fresh concrete in practice, but not based on the resulting porosity of concrete.

In this paper, four commonly used AEAAs in China are investigated for their air entraining abilities in cement pore solution (CPS), their effects on the air entrainment in fresh concrete and final porosity in hardened concrete. The aim of this paper is to present a correlation between the influence of AEAAs on fresh and hardened state concrete, and provides a reference for the development and application of AEAAs especially in China for the future. To quantify the complex formation and the resulting stability of bubbles in solution, the performance of AEA in CPS is also investigated.

2. Materials and Methods

2.1. Materials

Ordinary Portland Cement (OPC) is purchased from Sichuan Esheng Group, Si-chuan, China. Fly ash is purchased from Chengdu Lingyun Fly Ash Comprehensive Utilization and Development Co. Ltd, Sichuan, China. Both are used as per supplied. Their chemical compositions and physical properties are shown in Table 1. Fine aggregates is crushed limestone (fineness modules = 2.7, Table 2). Coarse aggregate is also crushed limestone, with a continuous grading of 5/20 mm. The superplasticizer (SP) and 4 different AEA (Table 3, Figure 1) employed are provided by Shijiazhuang Chang’an Yucai Building Material Co. Ltd, Hebei, China and used as supplied.

| Table 1  | Chemical and physical compositions of cement and fly ash |
|----------|---------------------------------------------------------|
|          | SiO₂ (%)  | Al₂O₃ (%)  | Fe₂O₃ (%)  | CaO (%)  | SO₃ (%)  | MgO (%)  | K₂O (%)  | Na₂O (%)  | LOI (%)  | Specific surface area (cm²/g) |
| Cement   | 22.1      | 4.8        | 3.1        | 64.3     | 2.1      | 1.9      | 1.0      | 0.2       | 1.6      | 3410                                      |
| Fly ash  | 54.1      | 27.4       | 6.4        | 2.2      | 0.1      | 0.8      | 1.6      | 0.4       | 2.9      | 3600                                      |

| Table 2  | Sand gradation |
|----------|----------------|
|          | Sieve diameter (mm) | Grader retained percentage (%) | Accumulated retained percentage (%) |
|          | 4.75   | 1.3 | 1.3 |
|          | 2.36   | 19.6 | 20.9 |
|          | 1.18   | 18.7 | 39.6 |
|          | 0.60   | 17.8 | 57.4 |
|          | 0.30   | 14.2 | 71.6 |
|          | 0.15   | 10.4 | 82.0 |
|          | 0.075  | 9.7 | 91.7 |
|          | Residual | 8.3 | 100.0 |

| Table 3  | Physical parameters of air-entraining agent |
|----------|-------------------------------------------|
|          | No.          | Main chemical type                      | Color   | State of matter  |
|          | AEA-1        | Sodium Abietate                         | brown   | liquid           |
|          | AEA-2        | Lauryl sodium sulfate                   | white   | powder           |
|          | AEA-3        | Sodium Abietate/Lauryl sodium sulfate   | yellow  | liquid           |
|          | AEA-4        | Sulfate compound air-entraining agent   | brown   | liquid           |
|          | AEA-5        | Triterpenoid saponins                   | brown   | liquid           |
Figure 1 Molecular structures of AEAs (a: Sodium Abietate; b: Lauryl sodium sulfate; c: Triterpenoid saponins)

2.2. Experiment method

2.2.1. AEA in CPS – Shaking experiment.
Water is added to OPC at a w/c of 2, mixed for 2 min and filtered under pressure to obtain the CPS. CPS is used immediately after production. A 15 mL 1 wt.% AEA–CPS solution is prepared, shake violently for 10 s and let stand. The total volume of the foam at 0 min, 15 min and 30min is observed and recorded[16].
2.2.2. Air entrainment measurement in fresh concrete.
Concrete mixes are prepared with a water to binder ratio (w/b) of 0.46 and 1 wt.% SP to maintain a slump of 180 mm. The mixture proportion is given in Table 4 and initial air content is controlled at 3.5 to 4.0 vol%.

Table 4 Mix design of concrete

| Material dosage (kg·m⁻³) | Concrete admixture content (%) |
|--------------------------|--------------------------------|
| Water                    | Cement                        |
| 165                      | 290                           |
| Fly ash                  | Sand                           |
| 70                       | 805                            |
| Sand                     | Stone                          |
| 805                      | 1025                           |
| Stone                    | GK-3000                        |

According to Chinese Standard GB/T 50080-2016, the air contents of fresh concretes are tested with a SANYO direct reading air content tester (SANYO, Japan). The air void structure of fresh concrete was tested by AVA3000 air-void analyzer.

2.2.3. Investigation on the porous structure of hardened concrete.
The porosity, i.e. hardened air void structure of the hardened concretes is obtained with a NELD-BS610 hardened concrete air-void parameters analyzer (Naierde, China) according to Chinese Standard SL 352-2006.

3. Results and Discussion

3.1. Air entraining performance of air entraining agent in cement pore solution

Figure 2 Generated foam volume with different AEAs added in CPS as a function of time
CPS contains high amount of electrolytes that can impart a viscosifying effect on the AEAs\cite{3,17,18}. Figure 2 displays the amount of foam generated and remained as a function of time in CPS when different AEAs are added. The initial amount of foam from CPS containing AES 1 to 4 are 13.5 mL, 47.2 mL, 43.8 mL and 27.1 mL respectively, i.e. measured foam volumes are: AEA-2 > AEA-1 > AEA-3 > AEA-4. From Figure 3, it can be observed that rate of foam loss of the AEAs at 15 min are 16.3%, 32.0%, 7.3% and 12.9%, respectively, which varied to 23.0%, 51.1%, 12.1% and 20.3% respectively at 30 min. AEA-1 is a rosin based air entraining agent with carboxylic acid groups. In CPS, a large number of electrolytes particularly calcium ions can interact with carboxylic acids to form insoluble calcium soaps. This results in poor foaming capability. However the insoluble calcium soap is adsorbed on the surface of the liquid film to increase the thickness of the bubble film and effectively prevents the aggregation and rupture of bubbles, stabilizing the foam\cite{4}. While having the highest amount of initial foam, CPS containing AEA-2 displayed the highest rate of foam loss as a function of time. This shows that sulphate type AEA may have the best air entraining performance, but when employed alone the introduced bubble type and stability are not ideal. In combination, sulphate and rosin AEA has excellent performance in air entraining ability and air stabilizing ability, as confirmed by the synergetic effect presented when AEA-3 is added. While having similar initial foam amount as AEA-2, the rate of foam loss for AEA-3 is the smallest. The anionicity and low molecular weight of SDS (AEA-2) allow the molecules to be agile and quick in arranging on the air-liquid interface, causing good initial foaming ability. However, as the bubble film viscosity is small (low thickness), coalescing of the small air bubbles occur rapidly and can quickly escape and rupture\cite{19,20}. From the observation, the presence of SDS gives good foaming ability (AEA-2) while rosin component (AEA-4) improves the foaming stability of the air-entraining agent. Moreover, SDS as a straight-chain alkane organic acid with a small and soft molecular structure can effectively fill in the void of rosin molecules to form a wedge-shaped structure that can transform into a stable bilayer as the molecules self-assemble\cite{21}. thus further increases the liquid film thickness and improves the stability of the foam.

AEA-4 is a triterpenoid saponin air entraining agent. AEA-4 has the highest molecular weight among the 3 single AEAs, thus is unable to form directional arrangement at the interface causing adsorption at the gas-liquid interface to be lowest. The presence of spatially distributed hydroxyl groups in the saponins glucose unit together with intermolecular van der Waals forces generates thick and elastic bubble films, in-creasing the stability of bubbles formed\cite{19}. 

![Figure 3](image_url)  
**Figure 3** Stability of foam generated by different AEAs in CPS
3.2. Effect of AEAs on the type of air bubbles and air entrainment in fresh concrete

Figure 4 Dosages of AEAs added to achieve the desired air content in fresh concrete (3.5%-4.0%)

Figure 4 shows the dosage of different AEAs when the air content of fresh concrete is controlled at 3.5%-4.0%. As can be seen from Figure 4, when the air content is roughly the same, the amount of AEAs needed are as follow: AEA-2 > AEA-3 > AEA-1 > AEA-4 (0.012%, 0.013%, 0.023% and 0.030% respectively), differing from that in CPS. This difference can be explained by the non-uniformity and complexity of the concrete system. In the process of mixing concrete, the existence of air bubbles is a balance between formation and destruction as particles and aggregates can ‘burst’ the generated air bubbles. Particularly for AEA-4, whereby air bubbles are stabilized by van der Waals forces, presence of ‘bursting agents’ can greatly destabilize the air bubbles. In-soluble calcium soap, compatible with the highly electrolyte rich concrete as formed by AEA-1 can effectively prevent the bursting of air bubbles. AEA-2 on the other hand, can migrates quickly to the gas-liquid interfaces to generate air bubbles rapidly, thus air entraining performance remain superior. Similar to in CPS, AEA-3 as a combination AEA is able to display both good air bubble formation and eventual stability.

Table 5 Air contents of fresh concrete containing AEAs, measured by pressure method and AVA method

| No.   | Air content measured by pressure method (%) | Air content measured by AVA (%) |
|-------|--------------------------------------------|--------------------------------|
| AEA-1 | 3.7                                        | 2.9                            |
| AEA-2 | 3.5                                        | 2.3                            |
| AEA-3 | 3.5                                        | 3.1                            |
| AEA-4 | 4.0                                        | 3.7                            |
Air contents of fresh concrete containing AEAs, measured by pressure method and AVA method are shown in Table 5, while Figure 5 presents the differences in measured air contents between these two methods. The air contents of the concretes measured by the AVA method is in all less than that measured by the pressure method as the former method only takes into account air bubbles less than 3mm, while pressure method includes all air bubbles present. The difference in air bubble content measured by the two methods is AEA-4 > AEA-3 > AEA-1 > AEA-2, indicating that the percentage of small air bubbles in concrete prepared with AEA-4 is the highest, while concrete with AEA-2 contain mostly larger air bubbles. As the presence of smaller air bubbles indicate better concrete performance, the air void structure of the concrete mixed with AEA-4 and AEA-3 may be the best, followed by AEA-1, and AEA-2. It is of interest to note that the amount of air bubbles below 3 mm is also the highest in AEA-4, indicating that saponin based AEAs are ideal for maintaining fresh concrete properties including workability.

Figure 6 shows the cumulative air content of the fresh concretes. For concrete containing air bubbles below 100mm, the order is as follow: AEA-4 > AEA-3 > AEA-1 > AEA-2. As expected, AEA-2 produced the largest percentage of large air bubbles (> 0.2 mm) and AEA-4 appeared to have the best
stomatal structure and air stabilizing ability, indicating that the air entraining property in fresh concrete is similar to that in CPS. The compound AEA-3 has the advantages of two AEAs, and the synergistic effect between the components can effectively improve the AEA’s air entraining performance and improve the air void structure of fresh concrete. There is little difference in the cumulative air voids in fresh concrete containing AEA-3 and AEA-4.

3.3. Influence of air entraining agent on air void structure of hardened concrete

Figure 7 shows the cumulative air void content of hardened concrete mixed with different air entraining agents at 28 days. When comparing Figure 6 and 7, the amount of air escaped from fresh concrete to its hardened state is about 10%, indicating that the air loss after first hour is consistent for all concretes, regardless of AEA types. Therefore, the main impact of AEAs on the final hardened concrete property may be determined from the initial air entraining effect. AEA-4 introduces the largest number of small air voids in hardened concrete, with AEA-3 coming close, followed by AEA-1 and finally AEA-2.

4. Conclusions

Here, we showed the performance of 3 commonly employed AEAs on their performance in concrete, both fresh and hardened state. As a reference, CPS was employed and it was found that air bubbles development in concrete or in concrete differs slightly, but can provide valuable information. It was found that AEAs can either generate air bubbles or stabilize them, rarely displaying both properties. Sulphate based AEAs may be the most ideal AEA types to generate in situ air bubbles, whereas stabilization depends greatly on the hydrophobicity and anionicity of the molecules or the formation of calcium soap. However, it is possible to formulate AEAs with both good foaming and air bubbles stabilizing properties when AEAs with different properties (e.g. sulphate + rosin based) are formulated together.

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