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Cement and Concrete Research 35 (2005) 1463–1471

Cement and Concrete Research

# Mechanisms of air entrainment in concrete

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Received 11 November 2003; accepted 15 July 2004

## Abstract

The advent of air-entraining agents is probably one of the most important technological advances in construction in the last century. It has been widely used to improve the freeze–thaw resistance of concrete, and to a lesser extent, the workability of concrete. Despite the overall successful application of air-entraining agents in concrete, problems in field concrete are not uncommon. The ability to consistently obtain target air-void systems in concrete is not trivial, and changes in raw materials, processing, or construction methods may significantly impact air entrainment. To address these potential problems in the field, a sound understanding of the mechanisms of air entrainment is essential. This paper attempts to synthesize available literature and field experience and provide a framework for understanding the fundamental aspects of air entrainment in concrete. Various parameters and influencing factors, such as concrete temperature, the physical and chemical characteristics of constituent materials, and mixing and placing techniques, are discussed.

*Keywords:* Adsorption; Air-entraining admixture; Air content; Stability; Temperature

## 1. Introduction

Ever since air entrainment was first discovered (by accident) in the mid-1930s, the concept of air-entrained concrete has become a rule, and not the exception in cold-climate concreting. Discovered by chance when a grinding aid used to enhance cement grinding ended up chemically entraining air in concrete and improving frost resistance in the field, air-entraining agents have had years of success in improving resistance to freezing and thawing damage (due to both internal distress and salt scaling) [1]. However, this success has not come without some turmoil as even today concrete producers wrestle with controlling air content in concrete, and the list of factors affecting air entrainment [e.g., temperature, cement chemistry, and supplementary cementing materials (SCMs)]. To fully understand the complexities of air entrainment, and more importantly, to apply this in practice, the mechanisms of air entrainment must first be understood.

Research has been devoted to the development of air-entraining admixtures (AEAs), the study of factors affecting the air-void system, and the correlations between air-void system and the corresponding freeze–thaw resistance. Mielenz et al. [2] discussed in detail the origins and evolution of the air-void system in concrete. Powers developed the concept of spacing factor of air voids, and this approach has been widely accepted to ensure the freeze–thaw resistance of concrete [3,4]. Zhang [5] studied the effects of different types of fly ashes and their dosages on the volume of air entrained, stability of air bubbles, and air loss with time with the use of different AEAs. The majority of the research has been placed on the practical aspects of air entrainment, with only slight emphasis on mechanisms of forming and stabilizing air bubbles in concrete. Bruere [6] discussed factors affecting the air entrainment in cement and silica pastes. Fagerlund [7] proposed three mechanisms that could lead to air-void instability in fresh concrete. Powers [8] also discussed in detail the process of air entrainment and various influential factors, although Powers did not address directly the complex chemical aspects of the bubble forming and stabilizing processes.

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doi:10.1016/j.cemconres.2004.07.026

Although air entrainment is a common practice, failure due to inadequate air entrainment is still common and has been reported in the literature [9]. A fundamental shortcoming of air entrainment today is that only total air content is typically specified, although as Powers [4] pointed out, air-void size and distribution contribute more to frost resistance. However, the extreme difficulty of obtaining the bubble size distribution in fresh concrete makes it only practical to measure the total air content as a quality control measure. The essential characteristics of air-void systems are typically only evaluated when called for by a specification (which is rare) or as a result of less than stellar field performance. These analyses of air-void size and distribution are almost always performed on hardened concrete specimens, although a reasonable index of air bubble size and distribution can be gleaned from fresh concrete using available commercial equipment.

Given that there are still problems in the field in properly entraining air and that so many factors influence air in concrete, it is imperative to understand how bubbles are formed and what makes them stable, unstable, or somewhere in between. The remainder of this paper discusses the factors that most affect air entrainment from a mechanistic perspective and is based on a synthesis of published literature and field experience.

## 2. Formation and stabilization of air voids in fresh concrete

Chemically entraining air in concrete is difficult to be categorized in the sense of a conventional chemical process. It can be viewed as an emulsion of air in the aggregate–cement–water system or foam formation in the liquid phase and retained by the solid network, or both. This paper focuses on the overall air entraining process and no distinct classification will be made between emulsion and foaming. Similar to foams, air bubble formation and stability in fresh concrete should be considered as two separate processes that are equally important for the air-void system in hardened concrete. These two phenomena are discussed below.

Dodson [10] presented a comprehensive review of air entrainment in concrete, and Powers [8] described how the two primary processes in the mixing action generate air in concrete. One process proposed by Powers is infolding of air by a vortex action, like stirring a liquid. The other process is a so-called *three-dimensional screen* formed by the fine aggregates when the mass falls and cascades onto itself during mixing. Mielenz et al. [2] proposed four origins of air in concrete, which include air already contained in the system and air entrapped during mixing. Reviewing past literature on air entrainment revealed that it is clearly an extremely complex process, which is affected by many factors, including the mixing process, concrete mixture proportioning, fine and coarse aggregates characteristics, physical and chemical properties of portland cement, water amount and quality, dosage and properties of air-entraining agent, other chemical admixtures and SCMs, and a range of other parameters. Because it is such a complex phenomenon, the usefulness of any quantitative model to predict the air-void system characteristics is questionable. As such, the aim and approach of this paper are more qualitative, although some experimental data are cited.

Air bubbles in fresh concrete are inherently unstable. The interfaces between the dispersed air and the surrounding matrix contain free surface energy, and the thermodynamic tendency is to reduce the interfacial surface areas. Thus, all air bubbles have a lifetime (persistence). If concrete setting is severely retarded, lack of small air bubbles in hardened concrete may be expected, which is detrimental to the freeze–thaw resistance of concrete. From the point of foam instability, three fundamental physical mechanisms may lead to the collapse of air bubbles [11]:

1. Diffusion of air from a bubble (small, higher internal pressure) to a larger one (lower internal pressure) or into the bulk gas (or solution) surrounding the foam;
2. Bubble coalescence due to capillary flow leading to rupture of the lamellar film between the adjacent bubbles (usually slower than mechanism 1 and occurs even in stabilized system);
3. Rapid hydrodynamic drainage of liquid between bubbles leading to rapid collapse.

Because of the mechanisms behind the instability shown above, pure liquid cannot form stable air bubbles. For foams to be useful, they must have a reasonably long lifetime that is related to one or more stabilization mechanisms. The use of AEAs in concrete is a classic example of one of the applications of emulsion and foaming technology.

The three mechanisms of air-void instability in concrete described by Fagerlund [7] can be categorized in mechanism 1 listed above. Mechanism 2 discussed above can occur in fresh concrete as the vibration from consolidation may force air bubbles to come into contact and form a larger one. Mechanism 3 is not likely in fresh concrete because air bubbles in fresh concrete are immersed in water. Note that for a given air content in concrete, the larger the air-void diameter, the larger the spacing factor and specific surface area, and the lower the freeze–thaw resistance. Similar to emulsion stability, one can argue that physical agitation, like shearing (mixing) and rapid agitation (vibration), may also lead to the loss of air in concrete [12].

The hydration of portland cement is a complex and continuous process, and the rate changes with time. The mixing water surrounding air bubbles is continuously changing in solutes and concentrations. Cations ($Ca^{2+}$, $Al^{3+}$, $Na^{+}$, and $K^{+}$) and anions ($OH^{-}$ and $SO_4^{2-}$) show their presence in liquid phase and some of them may have high amounts at a certain period of time. These ions can affect the entraining and foaming ability and persistence of a surfactant system, positively or negatively. Fresh concrete is frequently agitated before it is placed and this facilitates the influence of ions on the stability of air bubbles. Other chemical admixtures, such as superplasticizers, can also work as an air promoter or inhibitor, depending on their specific chemical nature and the AEA used.

Chatterji [13] pointed out that the other type of AEAs, including visol resin, sodium adipate, sodium oleate, etc., do not reduce the surface tension of water. These agents react with the calcium hydroxide solution in the cement paste to form insoluble calcium salts. The salts accumulate at the interfaces between air, water and cement, and stabilize the air bubbles as the case in emulsion. However, the following discussion will mainly focus on the surfactant type.

## 3. Distribution of air-entraining agent molecules in fresh concrete

### *3.1. Properties of surfactants*

The discovery of AEAs is one of the most important technological developments in the history of concrete. AEAs are mainly mixtures of various surfactants. To understand the role of surfactants play in this process, it is important to learn their chemical properties. The basic chemical nature of surfactants is shown in Fig. 1 [14]. The chemical unit that has a strong attraction for the solvent (water) is called the hydrophilic head. The molecular components that have little attraction for water are called hydrophobic tails. The most useful chemical classification of surfactant is based on the nature of the hydrophilic heads, i.e., anionic, cationic, nonionic, and amphoteric (and zwitterionic). In the amphoteric group, the molecule contains or can potentially contain both a negative and a positive charge. Most of the modern AEAs are anionic in character because of the stability of the air voids generated with them [10]. The stability of air voids entrained using cationic or nonionic AEAs is questionable. The foaming mechanism will be discussed in latter sections.

### *3.2. Adsorption and absorption of surfactants on solid surfaces*

In the concrete system, the contribution of aggregates to the solid surface areas is negligible compared to the cementitious materials. The main components of portland cement are $C_3S$, $C_2S$, $C_3A$, and $C_4AF$ (and gypsum). It is reasonable to consider that cement particle surfaces contain charges and high free surface energy. The adsorption or absorption of surfactant molecules to the surfaces of cement particles and to the early precipitated hydration products to reduce the free surface energy is thermodynamically preferable. The potential of adsorption of ionic AEAs onto solid surfaces is high because of the charged head group of the surfactants used. It would be insightful if one could measure the surfactant adsorption isotherms in fresh concrete, but there are several factors that make this task very difficult. Typically, AEAs are composed of a mixture of surfactants with different molecular weights and the adsorption. The hydration of cement is continuous and more solid surfaces are appearing, whereas the old surfaces are changing their properties constantly. Furthermore, the ion types and concentrations in the water are constantly varying with time during the early hours. This time dependency of the bulk solution makes adsorption equilibrium variable, and a quantitative model is unpractical, if not impossible.

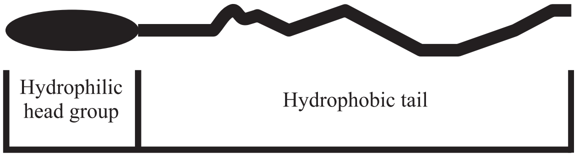

Fig. 1. The basic chemical nature of surfactants [13].

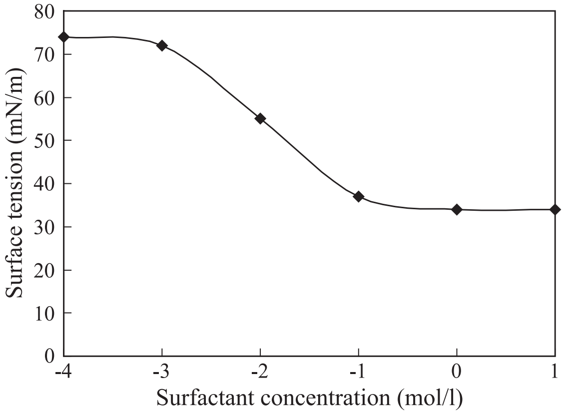

Fig. 2. The rapid change of surface tension over a relatively small concentration range [11].

### *3.3. Surfactants in the bulk liquid phase*

Apparently, to function as successful AEAs, the surfactants must be soluble or slightly soluble in mixing water. A number of anionic AEAs exist in the market, including soluble salts (usually sodium) of wood resins, wood rosins, lignosulfonic acid, sulfonated hydrocarbons, proteinaceous materials, and fatty acids [10]. The surfactant molecules in the solution help entrain air bubbles and stabilize them in the fresh concrete.

The foaming capacity of a surfactant depends primarily on its effectiveness to reduce the surface tension of the solution, its diffusion characteristics, its properties with regard to disjoining pressure in thin films, and the elastic properties it imparts to interfaces [14]. The addition of surfactants to water may significantly reduce the surface tension at water and air/vapor interface. Fig. 2 shows the effect of surfactant dosage in solution on surface tension [11]. Pure water has a surface tension of about 76 mN/m. It is interesting that at very low dosages, the surface tension of the solution is not reduced. This helps explain why a minimum dosage of AEA is required in concrete. The surfactants in the liquid phase, $S_l$, beyond the amount adsorbed on solid surface, are responsible for foaming behavior. For high dosages, there is a phenomenon called micelle formation that accounts for the limit of surface tension reduction. A micelle is the aggregation of surfactant molecules and may be viewed simplistically as structurally similar to solid crystal or crystalline hydrate. Above a certain surfactant concentration [critical micelle concentration (cmc)] the monomer concentration is almost constant and the micelle concentration increases with surfactant concentration. The micelles do not contribute to the reduction of surface tension. This likely accounts (partly) for the observation that there is a maximum amount of any admixture dosage beyond which there is no more increase in entrained air.

An equally important role that AEAs play is to stabilize the generated air bubbles. The combined Gibbs–Marangoni effect is the theory derived to explain the function that surfactant played in foam film formation and persistence [11]. From Gibbs adsorption equation, the surface tension of a liquid will decrease as the concentration of the monomer surfactant in solution increases (assuming positive adsorption) up to the point of surface saturation. The instantaneous (dynamic) surface tension at a newly formed surface is always higher than the equilibrium value. There is a finite time requirement during which the surfactant in the solution must diffuse to the interface in order to lower the surface tension. The time lag in reaching the equilibrium surface tension due to diffusion is generally known as the Marangoni effect, which explains why the diffusion properties and concentration of a surfactant is important. These two surface tension effects are usually complementary. Because the disturbance of air bubbles in concrete is unavoidable, the Marangoni effect is essential to maintain the integrity of air bubbles.

### 3.4. Surfactants at the water and air interfaces

The orientation of surfactant molecules in bulk solution is random. However, the adsorbed molecules have preferred orientations that tend to minimize unfavorable interactions between the liquid phase and the surfactant molecular sections. Fig. 3 shows the alignment of a monolayer of surfactant molecules at the interface between compressed air and surrounding liquid phase. The hydrophobic tails of surfactant molecules stick out of the solution to reduce the distortion of water molecules by the hydrophobic sections and thus lower the overall free energy of the system. The mutual repulsion between the hydrophilic heads of surfactant molecules reduces the attraction of the bulk liquid phase and a lower surface tension is resulted. Because of the electrostatic component of the repulsion force of ionic surfactants, their effectiveness to reduce surface tension is more significant than nonionic surfactants. The nature and concentrations of the surfactants determine the physical and chemical properties of the interface at the air bubble surfaces, including surface tension (equals to free surface energy) and stability. The electrostatic and steric repulsions between surfactants help stabilize air bubbles in the paste phase. Ions, organics, and polymers in the bulk solution also affect the properties of the interfaces through complex interactions with the orientated surfactant molecules.

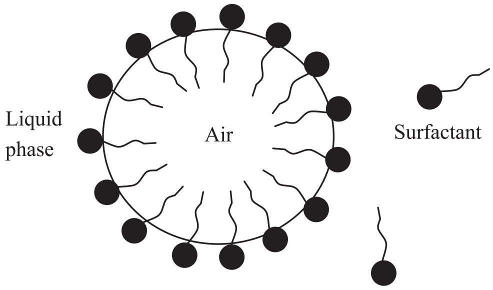

Fig. 3. Distribution of surfactant molecules at the water–air interface.

### 3.5. Surfactant molecules in fresh concrete

Based on the above discussions, the following equation is proposed:

$$A = A_s + A_l + A_b \tag{1}$$

where $A$—amount of surfactant added to the mixture system; $A_s$—amount of surfactant adsorbed or absorbed on solid surfaces; $A_l$—amount of surfactant in the bulk liquid phase; and $A_b$—amount of surfactant concentrated at the liquid and air interface.

Because of the continuing hydration of cement, the physical and chemical properties of the mixture system are changing constantly. Thus, the distribution equilibrium of surfactants in the three states should also be viewed as dynamic. The $A_s$ portion of surfactant contributes little to the air bubble formation and stability. The $A_b$ portion is responsible for forming and stabilizing the entrained air bubbles. The $A_l$ portion is essential because these molecules balance the surfactant molecules tied in $A_s$ and $A_b$, making them in a transient equilibrium state. These surfactant molecules also function as a “healing” agent for disturbed air bubbles through the combined Gibbs–Marangoni effect.

## 4. Factors affecting air entrainment in concrete

### 4.1. Mixing action and mixture proportions

Powers [8] described how air is entrained into concrete mixture during the mixing action. From the observation of movements of aggregates and paste in the mixer, he proposed that a vortex action (stirring) of mixer blades and three-dimensional screening of fine aggregates is essential in the air entrainment process. However, in the authors’ opinion, the characteristic motions of the various concrete components are quite complex, and such a defined division of processes may not be feasible or accurate. It is helpful to look at this complex foaming process from the aspects of work and energy.

The formation of air bubbles in fresh concrete creates new interfaces and thus free energy is put into the system by work (in the form of mechanical mixing). For the liquid/air interface, the surface tension value is equal to the free surface energy per unit area. Higher AEA dosages in the system reduce the surface tension values and bring higher amount of $A_1$ into the system. It is, thus, expected that higher volumes of air and more stable bubbles will be entrained with higher AEA dosages. Of course, the specifics of the mixing action and the concrete mixture itself will also influence how efficiently the work applied by mixing can be turned into free surface energy of air bubbles.

The effects of mixture proportions on air entrainment are quite complex. Air entrainment is a dynamic process in which new air bubbles appear and older air bubbles vanish at the same time. During mixing, the localized shear, compression, extension, twist, and compaction actions are affected by all components and their amounts in the mixture, including the existing air bubbles. All these action affect the bubble quantity and size distributions. To better grasp this process, air bubble formation will be considered as a combined process of gas emulsion and foaming.

Similar to the formation of an emulsion system, the mechanisms of bringing air into a concrete mixture can be considered as a combination of dispersion and condensation processes. Dispersion transforms the bulk air phase into dispersed small air bubbles. The mixing regime (equipment, revolution rate, mixing time, etc.) influences this gas emulsion process. The mixture of coarse and fine aggregates, cement particles, water, and other materials forms a three-dimensional system that influences the bubble size distribution and prevents the existence of a significant amount of large air bubbles. The free migration of air bubbles in the mixture is also hindered by the solid components in the system. The condensation process is relevant in that the solubility of air decreases when the pressure is decreased or other solutes increased. Like the phenomenon of cavitation, air may be released from water and form small bubbles during the mixing action. At the same time, tiny bubbles may be dissolved due to the local high pressure triggered by the mixing action.

In liquid emulsion technology, it is well known that a third additive is often needed to impart a reasonable stability of the system. These materials include simple electrolytes, natural resins and other macromolecular compounds, finely divided, insoluble solid particles or sols, and surfactants, which are soluble in one or both phases and significantly alter the interfacial characteristics of the system [11]. Along the same lines, components included and products formed in the concrete mixture will affect the bubble formation and stability accordingly. For instance, the variations of calcium ion concentration with time in the liquid phase may affect the air bubbles' formation and stability by changing the foaming and stabilizing properties of surfactants.

### 4.2. Role of paste in air entrainment

At rest, cement paste is a Bingham-type fluid, and its properties are defined by terms such as yield stress and apparent viscosity. As pointed out by Powers [8], the yield stress of cement paste prevents the escape of small air bubbles whose buoyancy forces are not large enough to break the bulk paste phase. The viscosity of the paste and diameter of bubbles determine how fast the air bubbles move upward according to Stokes' law. High viscosity can provide a cushion effect for air bubbles to absorb shocks from disturbances. Viscosity also slows down the potential coalition of adjacent air bubbles by working as a barrier. Thus, the rheological properties of cement paste directly affect the air-void system that is generated and stabilized.

In addition to the fact that surfactants are adsorbed on cement particle and aggregate surfaces, there are also interactions at the solid–liquid–air interfaces. Mielenz et al. [2] and Bruere [6] have observed the adhesion of air bubbles to cement particles. The inclusion of a specific surfactant to introduce the selective adhesion between solid particles and air bubbles has been widely used to segregate valuable minerals from gangue in an ore, which is called froth flotation. Fig. 4 shows the adhesion of air bubble and cement particle. The mass of cement particles helps disperse air bubbles in the mixture and reduces the tendency of floating to the surfaces. On the other hand, the floatation force of air bubbles decreases the possibility and rate of settlement of cement particles. Correspondingly, the tendency of bleeding and segregation is reduced with air entrainment.

### 4.3. Temperature of concrete mixtures

The effect of temperature on the foaming properties of surfactants depends on the nature of the specific surfactant. If its solubility changes significantly with temperature, a surfactant's foaming ability increases in the same direction as solubility [11]. For instance, long-chain carboxylate salts

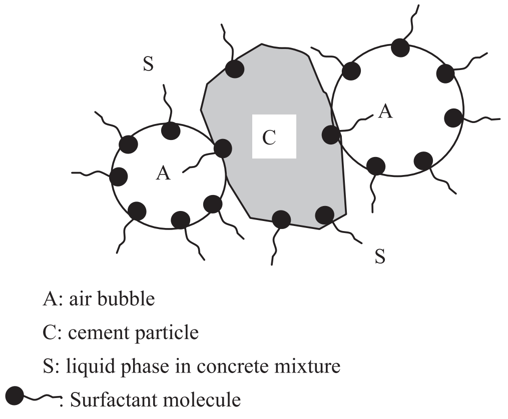

Fig. 4. Interaction between air bubbles and cement particles.

may have limited solubility and poor foaming properties in water at room temperature but will be more soluble and will foam more as the temperature increases. However, raising the temperature from 25 to 37 °C has been reported to reduce the stability of foams of nonionic surfactant solutions [15].

In the case of concrete mixtures, the effect of temperature on air entrainment is complicated by other factors. Powers [8] found that when an AEA is used, the air content generally diminishes as the temperature rises, although the water content is often increased to maintain constant slump. He has attributed this to the availability of water essential for air entrainment. However, in the authors' opinion, Powers neglected the possible chemical aspects of this phenomenon. As the hydration of cement is accelerated with increased temperature, the physical and chemical properties of concrete mixtures are different although they may have same slump values. The following four mechanisms are proposed to explain the temperature effect.

(1) Higher viscosity of concrete mixtures may result in lower air contents. Tattersall [16] reported that for the same slump values, concrete mixtures with higher temperatures probably have a higher apparent viscosity because of the faster hydration of cement particles. The viscosity of the paste phase can be viewed as the energy barrier to the air bubble formations. For the same amount and rate of work input, higher viscosity may reduce the total amount of entrained air, as well as bubble size and distribution.

(2) Polyvalent cations (i.e., $Ca^{2+}$ and $Al^{3+}$) in the liquid phase alter the foaming property of surfactants, especially ionic types. Dodson [10] found that the AEAs based on the alkali salts of wood rosins and resins react almost immediately with calcium ions to form insoluble calcium resonates or rosinates. These salts are capable of entraining air into the system because these insoluble solid particles or sols can help stabilize the gas emulsion, as mentioned above. With an increase in mixture temperature, the tendency and rate of insoluble AEA salt sols to coagulate and precipitate become higher and the foaming ability is lessened. In addition, when an excessive amount of electrolytes are in the solution, especially polyvalent ions, they may greatly reduce air bubble stability by reducing the electrostatically induced disjoining pressure. Disjoining pressure is the repulsion between the approaching electrical double layers formed around air bubble surfaces and helps prevent close approaching and then coalescence of bubbles.

(3) The hydration products in concrete mixture may adsorb or even absorb AEA molecules from the liquid phase and affect the stability of existing air bubbles. The hydration of cement is significantly accelerated with increased temperature. The hydration products increase the solid surface areas in the system and thus the surfactants adsorbed ($A_s$). Ettringite is known to have a charged surface and it is possible that some surfactants are strongly adsorbed from the liquid phase. With the decreased amount of surfactants as $A_1$ and $A_b$, less air will be entrained and stabilized in the system. The argument can be extended to explain the decrement of air contents with mixing time beyond a certain period. With a less amount of AEA in liquid phase, the amount of air bubbles generated is less than that lost in the mixing action.

(4) It is well known that the solubility of air in water decreases with an increase in water temperature. For an air-entrained fresh concrete mixture, an increase in temperature drives out the dissolved air in the water and it is natural for the air molecules to nucleate at the existing air bubbles, which is the shortest path (other than escaping into the atmosphere). Because there is no interaction between air molecules and water vapor, one can deal with them separately. For the air molecules, the pressure can be calculated using:

$$pV = nRT \tag{2}$$

For the vapor phase, the pressure is described using the Kelvin equation [17]:

$$p = p^* e^{-2\gamma V_m/rRT} \tag{3}$$

where $p^*$ is the vapor pressure of the liquid in the absence of an additional pressure, $\gamma$ is the surface tension, $V_m$ is the molar volume, $r$ is the radius of the air bubble, $R$ is the gas constant, and $T$ is temperature in Kelvin. Considering an air bubble in the fresh concrete, with an increase of temperature in concrete, $n$ and $T$ *increase in Eq. (2)*. Similarly, $\gamma$ and $T$ increase in Eq. (3). These changes require a concurrent change in $p$ or $V$ or both. Because the paste pressure balancing the internal pressure of air bubbles is the accumulation of atmospheric and gravitational forces, it may only change slightly due to the increase of viscosity of the paste. As a result, the bubbles have to expand their volume quite significantly. As mentioned above, air bubbles larger than certain sizes may be destroyed during mixing, transportation, and placement. At the same time, new bubbles are difficult to generate due to reason listed in (1). The final outcome is the decrease of entrained air content and larger bubble sizes in fresh concrete whose temperature is higher than when initially mixed.

In the authors' opinion, mechanisms 2, 3, and 4 above are more significant than mechanism 1.

### 4.4. Quality of mixing water

The foaming property of surfactants can be affected by the impurities present in the host solution. Inorganic electrolytes are most effective with ionic surfactants and polar organic additives can affect all types of surfactant [11]. Macromolecular materials can also influence the formation and stability of air bubbles. It is difficult to generalize their effects. If potable water is used as mixing water, the effect of impurities on air entrainment is negligible because of their tiny amounts. However, water with significant impurities present in it may have an effect (positive or negative) on air entrainment. For example, algae-contaminated water increases air content most likely because the organics help stabilize air bubbles [1]. The high concentration of polyvalent anionic ions, e.g., $Ca^{2+}$ and $Mg^{2+}$, in highly alkaline wash water from truck mixers and very hard water decreases the air content in concrete.

## 5. Observations of air entrainment in fresh concrete

### 5.1. Air entrainment decreases with an increase of cement fineness

The manufacturer-recommended AEA dosages are based on the mass of cement (or cementitious) materials in a given cubic meter of concrete. For the same amount of cement, an increase in cement fineness enhances the amount of surfactant adsorbed on solid surfaces, $A_s$. Thus, a less amount of AEA molecules is available for the air bubble formation and stabilization. The increment of fineness of cement particles also increases the hydration rate. Similar to the discussions about temperature effects, one could expect the loss of entrained air content is faster in concrete mixtures with Type III cement than with Type I cement.

### 5.2. Fine and coarse aggregates influence air entrainment

In addition to the three-dimensional screening effect discussed by Powers, aggregate shape, gradation, surface properties, and amounts also affect the size distribution of air bubbles by influencing the shearing and impact actions in the system during mixing. An increase of fines passing sieve #100 decreases air content probably because of the decreased air bubble sizes caused by the shear action of fines whose sizes are close to air bubbles. On the contrary, the gradations of sand between No. 30 and 100 promote the persistence of small air bubbles. Crushed rocks in concrete mixtures generate more impact and shear than river gravels during mixing and smaller air bubbles are formed. For the same amount of AEA in the system, smaller bubble sizes indicate lower air contents.

### 5.3. Slump of concrete mixtures affects air contents

As discussed above, slump is related to the yield stress of concrete mixture. Yield stress and viscosity of concrete mixtures act as energy barriers for air bubble formation. The higher is the slump, the easier is the gas dispersion in the mixture and probably larger air bubbles would result. An increase in slump from 75 to 150 mm (with all other mixture parameters remaining the same) will increase the air content [10]; however, above a slump of 150 mm, the large air bubbles becomes less stable due to buoyancy forces and the air content drops.

### 5.4. Temperature affects the effectiveness of air entrainment

An increase of concrete temperature from 21 to 38 °C may reduce air contents by 25%, whereas from 21 to 4 °C can entrain 40% more air [10]. The low temperature (4 °C) decreases the yield stress and viscosity of concrete mixture through lowering of viscosity of water and lessening hydration products at the very early age. Thus, more surfactant molecules are available for foaming and the effectiveness is also improved with the absence of high calcium concentration.

### 5.5. Mixer type and mixing time affect air contents

The mixer type affects how fast the air is dispersed in a given mixture. With the specific mixture proportions, the mixing actions (shear, torque, compression, tension, squeeze, and other action) largely determine the size distributions of air bubbles. Furthermore, the mixing actions and their effects are influenced by the relative amount of concrete in the mixture as small loads receive less stirring and larger impact. As a result, less air is entrained. Worn mixing blades are less efficient in dispersing air into the system, and a longer mixing time is needed for a specified air content.

As pointed out in the early section of this paper, air bubbles generate and vanish during mixing. Within the initial minutes, more air bubbles formulate in the system than those that break down or leave into atmosphere. When the dynamic equilibrium is achieved, the maximum air content available for the system under a certain mixing condition is achieved. Apparently, more powerful mixers need less time to obtain the desired air amounts.

### 5.6. Transportation, consolidation, and pumping affects air contents

Because air bubbles in fresh concrete exist in a transient state, any agitation from manipulations before setting may affect the air-void system. As for the mechanisms discussed above, undesirably long hauling time may cause loss of air contents up to 1–2% [1]. Hover [12] has pointed out the potential for additional air loss due to over-consolidation by vibrators. Hover and Phares [18] also found that the typical loss of air caused by pumping is around 1–1.5%. The use of bucket and conveyor was also found to cause loss of air from fresh concrete. The variations in air contents are generally greater between concrete mix trucks than within a single truck. Lessard et al. [19] found that vertical pumping enlarged spacing factor more significantly than horizontal pumping. Loss of small bubbles due to high pumping pressure, coalescence of small bubbles to form larger ones during descending, and effect of suction were proposed to explained the observed variations of air-void system [19].

### *5.7. Use of SCMs increases AEA dosages for required air content*

The use of SCMs in concrete has become almost the rule, and not the exception, due to improved durability, long-term strength, improved workability, and reduced cost (in most cases). Unfortunately, the absorption of AEAs by SCM particles often makes entraining air difficult and failure to meet the specified requirements is not uncommon if the AEA dosage is only based on the manufacturer's recommendations, which are typically based on pure cement systems (without SCMs). For instance, Zhang [5] has found that the inclusion of fly ash in concrete increases the AEA dosages from one to five times that required in ordinary portland cement concrete.

Two facts may help explain the observation. The SCM particles normally have higher surface areas than portland cement grains. In addition, a small amount of fly ash sometimes may have cenospheres (complete hollow sphere) and plerospheres (packed with numerous small spheres). Furthermore, the burning temperature of coal is lower than the sintering temperature of cement, and fly ash normally has a higher value of loss on ignition (LOI). The carbon content of fly ash is usually thought to be highly adsorptive. Modern combustion zone modifications for $NO_x$ control are producing more ashes with high residual carbon contents [20]. LOI is usually adopted by concrete practitioners to address the carbon problem in fly ashes. However, the effectiveness of using LOI as a sole indicator of air entraining ease was challenged by Hill et al. [21]. More detailed research has been conducted to evaluate the absorption of AEAs by the carbon particles with different organic nature, surface chemistry, and size and shapes [22,23]. The adsorption of AEA is found to be related to the easy accessible carbon surface areas, external and internal [22]. It has been shown that the smallest ash particles adsorb AEA most significantly [23]. Class C fly ash has much higher specific carbon surface areas than Class F ash does. However, the seemingly worse scenario for Class C ash is offset by its lower LOI than Class F ash, due to the different coal ranks (sources) [23]. Many factors may affect the adsorption of AEA by fly ash, including coal source (coal surface nature), pulverizing process, combustion zone, collecting method (size distributions), and others. Thus, it is important to examine newly received fly ash through trial batches.

To address the adsorption problem of AEA by the carbon present in fly ashes, Hoarty and Hodgkinson [24] described a unique AEA that did not suffer air loss over extended mixing. Sodium octnoate, more polar than sodium deconoate, is included in the agent, although the former has no air-entraining ability. Sodium octnoate is preferentially adsorbed onto the carbon surface to satisfy its activity and more sodium deconoate remains in the solution and is available for air entrainment [24].

Another potential effect is the change of the solute concentrations in the liquid phase of concrete mixture with the replacement of fly ash. The pore liquid extracted from cement–fly ash pastes had much higher calcium ion concentrations 2 h after mixing than pure cement paste. As discussed above, the calcium ions can affect the foaming ability of certain AEAs. Other ion concentration changes may possibly also play a role in air entrainment.

### *5.8. Other chemical admixtures affect air entrainment confoundedly*

As mentioned above, many inorganic electrolytes and polar organic materials influence the foaming ability of surfactants. Because of the complexity of modern AEAs and other chemical admixtures, it is impossible to generalize the effects of their interactions with surfactants on air entrainment. The compatibility of the admixtures should be experimentally examined if the effects of such combinations are not known in advance. Most organic chemical admixtures will increase air entrainment partly because they may reduce adsorbed AEA molecules on solid surface through competition, such as superplasticizers. In addition, macromolecular materials may help stabilize the dispersed air bubbles. Furthermore, some high-range water reducers themselves may have the air-entraining potential. However, the addition of straight calcium chloride may tend to reduce the amount of entrained air due to the precipitation of surfactants in the solution by formation of insoluble salts.

## 6. Summary

Air bubble entrainment and stability in fresh concrete is an extremely complex problem. The inability to routinely characterize air-void systems in fresh concrete in the field makes it even more important to understand the effects of many underlining factors, at least to a qualitative degree. Every component in concrete mixtures, including portland cement, aggregates, water, and admixtures affect the air-void system to varying degrees. On top of this, the use of different mixers, the batch quantity, the placing methods, and other operations affect air entrainment. This paper attempted to explain the relevant mechanisms governing air bubble production and stability and to provide some guidance for understanding and controlling the air-void system in field concrete. This is clearly a complex issue, and it is hoped that this paper has shed some light on the key factors influencing air entrainment in concrete.

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