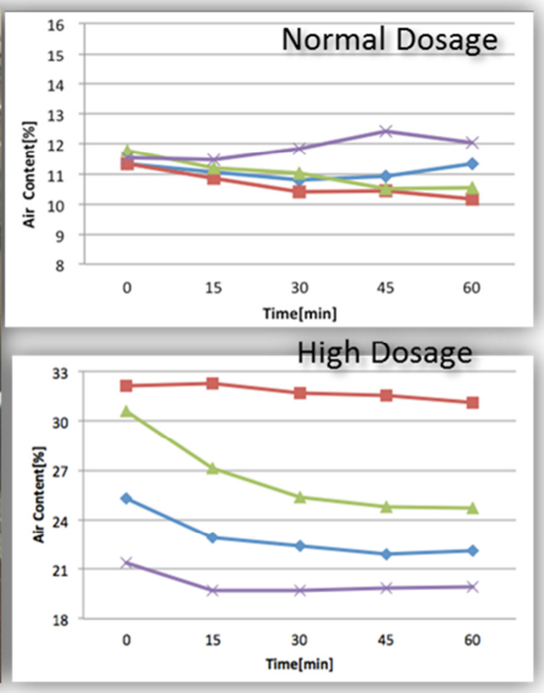

Stability of air bubbles in fresh concrete

Master of Science Thesis in the Master's Programme Structural engineering and Building Performance Design

QI YANG

Department of Civil and Environmental Engineering
Division of Building Technology
Building Materials
CHALMERS UNIVERSITY OF TECHNOLOGY
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Master's Thesis 2012:99

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Examensarbete / Institutionen för bygg- och miljöteknik,
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Cover:
Mortar mixer and results from the air content measurement

Chalmer reproservice / Department of Civil and Environmental Engineering
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ABSTRACT

The use of air-entraining agents to (AEAs) improves not only the freeze-thaw resistance of concrete but also the properties of fresh concrete, such as the flowability, the resistance to segregation, the resistance to bleeding, and the improved finishing quality. However, the key question is how to properly entrain the desired air bubbles and how these can be stably kept in the concrete (from fresh to hardened state). There are many factors in the procedure of concrete production that can influence the air bubbles in concrete and it is therefore important to understand the most influencing factors on air bubble stability.

In this study, four kinds of air-entraining agents, including synthetic (SikaAer-S, called as Sika-S) and natural ones (GYQ, Sika 88L and BASF Micro Air), were studied and compared with regard to their ability to entrain air and stabilize it. In these experiments, gravimetrical method was used to measure the air content and the stability of air bubbles in fresh concrete during one hour while the air void analyzer was used to measure the air void system including the air content and size distribution. The measurements were taken both at normal dosages and the maximum dosage of AEAs. The results of this study primarily show that Sika-S performances well in entraining and stabilizing air bubbles at a high dosage. GYQ was good in stabilizing the air bubbles but cannot entrain as much air as Sika-S.

To further study the influence of entrainment and stability in fresh concrete the effect of three kinds of cementitious materials were investigated at the maximum dosage. It seems that the cement with higher alkali content leads to increased air entrainment. While the cement blended with slag produces better air void system. At this time, it can be seen that although the total air content by GYQ is less than Sika-S, the content of efficient air bubbles are almost the same.

Based on the results in this study, it is possible to take the advantage of each material in cooperation with air entraining agent for entraining and stabilizing desired air bubbles.

Key words: air entrainment, AEAs, air bubbles, stability, air size distribution, cementitious materials

Contents

Preface

In this study, mortar tests have been done with four kinds of air entraining agents. The tests have been carried out from January 2012 to March 2012.This laboratory work is an important part of the project which gives me a data-based way to study the characteristic of bubbles in fresh concrete. The project is carried out at the C. Lab of Thomas Concrete Group AB and Chalmers University of Technology, Sweden.

I would like to thank my supervisors, Tang Luping and Ingemar Löfgren; they helped me a lot during this project work. I would also like to thank Oskar Esping who gave me a lot of help during the laboratory work. Furthermore, I appreciate the helps I got during this project work.

Göteborg June 2012

Qi Yang

Notations

V_{air}	as the air content determined by volume
ρ_{dry}	as the density of the fully dry material
ρ_{cement}	as the density of cement
$\rho_{agg.}$	as the density of aggregate
ρ_{water}	as the density of water
ρ_{bulk}	as the density of the container
M_{cement}	as the weight of cement
$M_{agg.}$	as the weight of aggregate
M_{water}	as the weight of water
M_{bulk}	as the weight of the container
$^{w}\!/_{c}$	as the water cement ratio

1 Introduction

1.1 Background

Air entrainment was first discovered in the mid-1930s by accident, after that the technology of entraining air in concrete was widely used to improve the freeze-thaw resistance of concrete, especially in cold-climate regions. [Kosmatka (1994)] Air entraining agents (AEAs), which can be based on natural resins (for example vinsol) or synthetic surfactants, were added to the concrete mix to increase the controlled quantity of air in the form of microscopic bubble in cement paste. From the first usage of air entrainers until now, many different kinds of air entrainers have been developed. However, regardless of what kind of air entrainers, they all have similar properties or functions, that is, all of them are powerful surfactants. The intention of using AEAs is to get more stable and uniform air bubbles with small sizes homogeneously distributed in the cement paste.

The fine air bubbles (the diameter smaller than 300 µm) in concrete can improve not only concrete freeze-thaw resistance but also the workability of fresh concrete. Owing to the improvement of workability of fresh concrete, the paste content in concrete can be reduced, benefiting both environmental conservation and hardened properties of concrete, such as reduced shrinkage and creep as well as reduced permeability.

In practice, however, the air bubbles in the concrete are very sensitive. There are many factors that can influence air content and the air void system in the concrete such as: paste composition; temperature of concrete mix; other chemical admixtures; mixer type and mixing time; and even the quality of mixing water. All of these factors make the process of entraining air more complicated. In addition, the air is also influenced by processes such as transportation, pumping, and compaction. So this project studied not only on how much air that can be entrained in the fresh concrete by using different kinds of AEAs but also on how good the entrained air void system were.

Today, many companies and research organisations are investigating how to entrain more air bubbles with better air void system, how to make the air stable in concrete, and which factors influence the air in concrete. By these investigations, a better understanding of the principle of the air entrainment in concrete will be achieved.

1.2 Purpose

The project aims at investigating the stability of air bubbles in fresh concrete. The results from this project is as the first step to find the best AEA for entraining the high volume of air bubbles with satisfactory stability and good air void system in fresh concrete. And then it is possible to discuss the sustainable way to improve the properties of the fresh concrete by replacing fine particles and fillers with air bubbles so as to reduce cement content in concrete.

1.3 Method

A literature study was conducted parallel with laboratory work. In the laboratory study, mortar tests with four kinds of AEAs were studied with regard to the stability of entrained air. Furthermore Air Void Analyzer (AVA), an apparatus able to measure the air void characteristics of fresh concrete, was used to measure the air content, specific surface areas, spacing factor and the size distribution of air bubbles. This provides a way to study the changes of the air bubbles regarding their content and size distribution in the fresh concrete with time.

The following methods were used during the laboratory work:

- Mortar tests, where the total air content was measured immediately after mixing and then every 15 minutes up to 1 hour. These measurements included two air entrainment levels: the normal air content and the maximum air content.
- Mortar tests to find the maximum air content for each of the four AEAs investigated.
- The air void system was studied by measuring the specific surface area, spacing factor and the size distribution with the “Air Void Analyzer” (AVA). These measurements were on normal air content as well as on maximum air content.

1.4 Limitations

The investigation was limited to mortar test. The fine aggregate used was sea-dredged sand with a maximum aggregate size of 2 mm. The *w/c* was chosen to 0.5. Since all the AEAs used in this study were either in the form of powder or in high concentration, which are hard to measure accurately, all the AEAs were diluted before used. The liquid ones were diluted tenfold and the powder one was made into solution before used. In order to get a normal air content which is around 5% in concrete and around 11% in mortar by volume, the dosage of diluted AEAs was around 0.3% of the cement content by weight. The temperature in the laboratory was around 19°C. The temperature of water in AVA was 22°C ± 2°C during the test.

2 Air Bubbles in Fresh Concrete

2.1 Function of air bubbles in concrete

2.1.1 Function of air bubbles in hardened concrete

The concrete paste is the mixture of cement and water. After their reaction the concrete will become hardened along with the time. Some of the remaining water in concrete would be lost by evaporation left with capillary pores, which will in turn absorb water from the exposure environment. When the temperature drops below zero, the water in the capillary pores will freeze. The freeze leads to an expansion (about nine percent) in volume, which introduces hydraulic pressure in the unfrozen water in the fine pores. When this pressure exceeds the tensile strength of paste or aggregate the concrete will start to deteriorate in the form of scaling or cracking. This is significant in a moist condition since the capillary pores would fully filled with water from environment left less space for filling or transfer of unfrozen water due to the expansion of ice formation. [FHWA Publication No. HIF-07-004 (2006)]

If there are air bubbles in the concrete, these bubbles or voids can hardly be saturated by capillary absorption. Thus the bubbles supply the spaces for unfrozen water to fill in under the expansion of ice formation in capillary pores. If the distance between air bubbles is short enough, the hydraulic pressure can easily be released when the unfrozen water flows to the bubbles.

So the main reason for entraining air in concrete is to improve the freeze-thaw resistance of hardened concrete. To achieve this, there will be many air bubbles in the concrete, and the effective bubbles, the air bubbles that can protect concrete from damaging during freeze thaw cycles, will generally be in the range 0.02-1 mm. And the spacing factor ($\bar{L}$), which is defined as the average distance from any point in the paste to the edge of the nearest void, should not exceed 0.2 mm. The fine air bubbles in concrete proved space for water/ice expansion and relieve pressure on the surrounding concrete. The air entrainment however leads to a reduction in strength of the concrete. Each 1% of entrained air in hardened concrete would lead to the reduction of 5% in strength. [Mindes et al. (2003)]

2.1.2 Function of air bubbles in fresh concrete

Air entrainment in fresh concrete can also improve the workability and cohesiveness of fresh concrete. The fine air bubbles in fresh concrete act as many fine aggregates with low friction and elastic which form a lubricating layer around solid particles so as to improve the workability such as flowability, resistance to segregation, resistance to bleeding, improved finishing quality, etc. So entraining more fine air bubbles with stability can reduce the amount of fine particles such as cement and water required on the same slump condition in concrete. This is a more sustainable way which benefits both environmental conservation and hardened properties of concrete, such as reduced shrinkage and creeps and reduced permeability due to reduced content of cement paste. Moreover by reducing the water in concrete, this partially offset the reduction of strength in hardened concrete caused by air entrainment.

2.2 Formation and stabilization of the air voids in fresh concrete

2.2.1 Mechanism of air entrainment

Air bubbles are actually not formed by air entraining agents but stabilized by them. However air bubbles formation and stability in fresh concrete are considered as two separate processes that are equally important for the air void system. One is air entrainment in fresh concrete which is by the mixing process. [Powers (1968)] Another is air stabilization which is achieved by adding AEAs which form a protective film around the air bubbles. There are a lot of factors that can generate and influence air bubbles in concrete but these air bubbles are inherently unstable. The interface between the dispersed air and their surrounding contain surface energy. So there is a tendency to reduce the interfacial surface area, which can be explained by thermodynamic theory. Without the presence of AEAs, the small air bubbles (higher internal pressure) tend to coalesce to form larger bubbles (lower internal pressure) which have a greater tendency to escape from the paste due to the much lower density. In addition, the capillary flow leads to rupture of the lamellar film between the adjacent bubbles; rapid hydrodynamic drainage of liquid between bubbles leading to rapid collapse. [Myers (1999)]

All of these physical mechanisms discussed above indicate that pure liquid cannot form stable air bubbles. The use of AEAs in concrete is an efficient way to stabilize the air bubbles in concrete.

As the AEA molecules insert into the cement paste, the mutual attraction between water molecules is reduced. And the absorbed AEA molecules at the surface of the bubble form a film, with their polar heads in the water phase (hydrophilic head group) and hydrophobic tail in air bubbles. If the molecule is charged, the bubbles can contain both a negative and a positive charge. The electrostatic repulsion keeps bubbles separated and prevents coalescence. [Dodson (1990)]

2.2.2 Air entraining agent in fresh concrete

Generally, a distinction is made between two kinds of air in concrete: one is entrapped air (natural) and the other is entrained air. The entrapped air is created during the mixing but is not wanted; it generally has a size more than 1 mm in diameter. Another is entrained air (designed) which is expected with the size 10 to 100μm in diameter. This type of air entrainment is needed for freeze-thaw protection. To achieve this, air entraining agents are used to entrain or stabilize more of the desirable air. Normally, there are three categories of AEAs: wood-derived products, vegetables acids, and synthetic detergents. Generally speaking, the synthetic ones generate air quicker than the organic ones; however, the organic ones show better compatibility with other admixtures than the synthetic ones. [Whiting (1998)]

Regardless of how many categories of AEAs, they are mainly mixtures of various surfactants. They stabilize air bubbles in concrete by changing the surface tension of the mixing water and act at the air-water interface within the cement paste. Their molecules always have hydrophilic and hydrophobic groups, by which it becomes orientated into the aqueous phase with the hydrophobic group inward toward the air. This also reduces the surface tension of the water which makes it easier to form the air bubbles in the cement paste. At the same time the formation of air in the cement paste is more stable and uniformly dispersed because of the “protection” around it (Figure

2.1). In fresh concrete the surfactants can be adsorbed and absorbed on solid (cement particles) surface, can be adsorbed at the water-air interfaces and can be soluble in mixing water. The amount of surfactant adsorbed or absorbed on solid surfaces contributes little to the air bubble formation and stability. The amount of surfactant concentrated at the liquid-air interface is responsible for forming and stabilizing the entrained air bubbles by orientating at the interface to minimize the unfavourable interaction between them. The amount of surfactant soluble in liquid is also essential because these molecules can balance the surfactant molecules adsorbed or absorbed on solid surfaces and at the water-air interface, which makes them in a transient equilibrium state. [Lianxiang and Folliard (2005)]

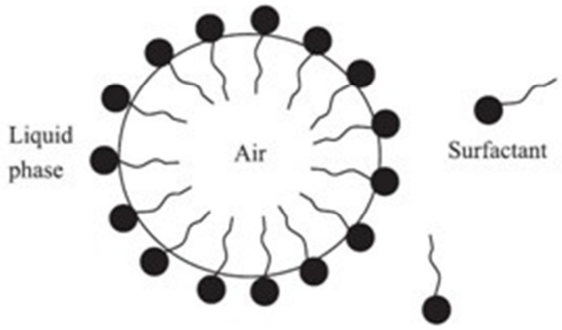

Figure 2.1 Stable air bubble with AEA [Lianxiang and Folliard (2005)]

2.3 Factors affecting air entrainment in concrete

2.3.1 Mixing

As mentioned above, air bubbles in concrete are firstly entrained by mixing process. Hence, the mixing is important factor which together with the aggregates can affect air entrainment in concrete, since the large air bubbles can be split into smaller ones by the movement of aggregates in the mixer.

From the viewpoint of work and energy, the formation of air bubbles in fresh concrete can be explained as follows: The mixing action gives the energy to the fresh concrete to create the interface between air and water and form the large air voids, and then split them into small voids. However, there is a tendency that the small air voids coalesce into larger ones. From the energy viewpoint it is clear that for the same volume of air, the one contains small air voids has a larger specific surface area and therefore higher energy than the one with large air voids, the latter can always more easily escape from the paste due to its larger buoyant force. So the mixing action (mixer, mixing time, revolution rate, etc.), can affect how much energy can be turned into free surface energy of the air bubbles which balance the surface tension of the air bubbles. For example, mixing with longer time can of course entrain more air in fresh concrete by applying more work on the paste.

2.3.2 Mixture

The concrete mixture itself also plays an important role in the air entrainment and the following factors influence the air:

- ***w/c* ratio**

Since the air bubbles must be formed in water, if the *w/c* ratio of the paste is too low, it is hard to entrain air in the paste. On the other hand, if the *w/c* ratio is too high, the small air voids can easily become large ones and then escape from the paste. It has been reported that with the increased *w/c* ratio, the spacing factor in hardened concrete will increase and the air void system become worse. [Yan Shang (2010)]

- **Aggregate**

The characteristics and grading of aggregates have also significant influence on air entrainment. In paste it is more difficult to entrain air because the entrained air is affected by buoyancy and there are no particles that can trap the air bubbles. In mortar and concrete, because of the addition of aggregates, the fine aggregates can form a space to hold the air bubbles and prevent them from escaping. Furthermore, aggregate with a sharp shape, like crushed stone, will entrain less air than gravel. The sharper the aggregate is the harder for the air bubbles to attach on it. [Dodson (1990)]

- **Cement alkali level and supplementary cementitious material**

The air content increases with increasing alkali level in the cement. This is because the alkali environment in cement paste allows the AEAs to create more air. However, high-alkali environment is not good for stabilizing the air bubbles and it also influence the air void system.

Fly ash, ground granulated blast furnace slag, silica fume and so on are used as supplementary cementitious materials frequently. Fly ash which contains carbon can attract and absorb the surfactants in AEAs. [Kqlaots (2004)] Slag is normally used at high dosage. It is usually finer than cement, so under the same condition using slag may decrease the entrained air but improve the air void system. Silica fume does not have significant influence on the air content and the stability of air bubbles; however, because of its fineness, greater amounts of AEA are needed. [Nagi et al. (2007)]

- **Chemical admixtures**

It is complex to conclude what and how the chemical admixtures affect the air entrainment. Most organic chemical admixtures like superplasticizer can increase the air entrainment since it can partly reduce the absorbed AEA molecules on the solid surface by competing with them. Other admixtures like retards, accelerators, etc., have minor effect on the air entrainment. However, today there are many kinds of AEAs like wood-derived acid salts AEA, vegetable oil acids AEA and synthetic detergents AEA, which may react with the chemical admixtures. This adds the difficulty on the study of the influence of chemical admixtures on the air entrainment.

2.3.3 Temperature

The temperature of mixture can affect the air entrainment by many aspects. First of all, as it is well known that higher temperature of water leads to the lower solubility of air in water. Secondly, as Tattersall (1976) reported, at the same slump value the mixture with higher temperature always gets higher viscosity and for the mixture with higher viscosity entraining air will become more difficult. How temperature and pressure affects the size of air bubbles in fresh concrete can be illustrated by the ideal gas law equation: $pV = nRT$; when p is constant, with increasing temperature the volume of air increases, resulting the bubbles with larger size which are unstable and, as a consequence, the total entrained air content will be reduced. Moreover, the alkali based AEAs react immediately with the calcium ions in the solution to form insoluble salts which are capable of stabilizing the air bubbles in the mixture. The increased temperature will increase the polyvalent ions in the solution which may react with the salts around the air bubbles and destroy the protection film around the air bubbles. The increased amount of electrolytes in the solution due to the higher temperature will reduce the stability of air bubbles by reducing the electrostatically induced disjoining pressure. [Dodson (1990)] At last, the hydration of the cement can be accelerated by increasing temperature. The hydration products will adsorb or absorb more AEA molecules from liquid phase. The mixture with less surfactant in the liquid phase will reduce the ability in forming and stabilizing the air bubbles. [Myers (1999)]

2.3.4 Other factors

- **Quality of mixing water**

As it mentioned above, hard water with high concentration of polyvalent ions like Ca^{2+} and Mg^{2+} will also decrease the air content.

- **Vibration**

If the time of high-frequency vibration is too long, the spacing factor of the air void system will increase. [Yan Shang (2010)] This is because the long-time vibration may make the small air voids merged together to form large ones.

- **Pumping**

The free fall and pressure are the main factors that influence the air entrainment when pumping concrete. In the pumping process, letting the concrete to free-fall always reduces the air content. However, most of the lost air bubbles are the coarse bubbles which contribute less to the durability of concrete. [Hover (1989)] The compressing and de-compressing of air bubbles in the pumping process can also alter the air void system. Sometimes the uncontrolled depressurization will lead the coalescence of the small air bubbles and let them escape from the mixture. [Fagerlund (1990)]

- **Surface finishing**

Finishing can affect the air content, but this is mainly at the surface and near-surface of the concrete. Finishing may cause the loss of air in concrete by an effect similar to the compressing and de-compressing as mentioned above. However, normally only coarser voids can be affected.

2.4 Some observations of air entrainment in fresh concrete

2.4.1 Effect of entrained air on concrete properties

The following effects of entrained air on concrete properties have been reported in the literature (based on Cement and concrete resources; & Lianxiang Du, and Kevin J. Folliard (2005)):

- The tendency of bleeding and segregation were reduced significantly with increased air.
- The bond between steel and concrete may decrease with increased air.
- The compressive strength will decrease by 5% for each 1% air increasing.
- The de-icer frost scaling is significantly reduced with increased air.
- The density of concrete decreases with increased air.
- The stickiness increases with increased air, which makes it harder to finish.

- The effect on permeability of concrete with increased air is very little. However, with increasing air content and equivalent compressive strength the *w/c* ratio need to be decreased, which then can lead to a reduced permeability.
- The slump increases with increased air content, approximately the slump increases 25 mm in slump for every 0.5 to 1 percentage increase in air.
- The thermal conductivity of the concrete decreases 1% to 3% per percentage increase in air.
- The expansion due to alkali-silica reaction has been reported to decrease with increased air.

2.4.2 Observations of factors influencing entrained air

The following observations of factors influencing entrained air have been reported in the literature (based on Nagi, M. A., Okamoto, P. A., Kozikowski, R. L., and Hover, K. (2007); Lianxiang Du, and Kevin J. Folliard (2005); & FHWA Publication No. HIF-07-004):

- Air content decreases with the increased fineness of cementitious materials.
- Fine aggregates can entrain more air than coarse aggregates
- When the slump is less than 150 mm, the air content increases with an increase in slump. However, above 150 mm, large air bubbles are more unstable due to buoyant force to escape from the mixture, which reduce the air content
- With increased temperature the air content decreases.
- Maximum air content is achieved at normal mixing time. Mixing too short or too long will both reduce the air content.
- Transportation may decrease the air content while pumping often decreases the air content.
- With the use of other cementitious materials, like fly ash and slag, a higher dosage of AEA is required compared with using Portland cement only in the same condition.
- The influence of other chemical admixtures for air entrainment is complex. Normally, most organic chemical admixture can increase the air entrainment.

3 Experimental Work

Mortar tests with different air entraining agents (SikaAer-S, GYQ, Sika 88 L, and BASF Micro Air) and different cements (Akmenes Cement and Anläggningscement) have been carried out and the total amount of air and the air void system have been studied.

3.1 Materials

3.1.1 Air entraining agents

Four kinds of air entrainers were used in the mortar test to compare their ability of entraining air and their formed air void system.

- **SikaAer-S (called Sika-S thereafter):** It is provided by Sika Sverige AB in Sweden. It is a transparent liquid and is based on a synthetic surfactant. The technical data of Sika-S is shown in table 3.1 below:

Table 3.1 Technical data of Sika-S

Colour and shape	Transparent liquid
Density	1.01 kg / dm ^{3}
pH value	Approximately 7
Chloride content	<0.10% by weight of the solvent
Alkaline Content, eq. Na_2O	<0.5% by weight of the solvent
Solids	Approximately 4.5%
Viscosity	Light liquid

  Sika-S was used by solution in this study which was diluted to 0.45% solid content.

- **GYQ:** It is a new air entraining agent developed and produced by Jiangsu Bote New Materials Co Ltd in China. It can be both powder and liquid. The main ingredient of GYQ is a kind of nonionic surfactant. For the transportation aspect, in this study powder type of GYQ was used. The technical data of GYQ is shown in table 3.2 below:

Table 3.2 Technical data of GYQ Powder

Colour and shape	Brown
Chloride content	$\leqslant$0.5%
Alkaline Content	6.0% ± 2%
Fineness	Residue on 0.315 mm $\leqslant$8.0%
Surface tension	49±3 mN/m
Water content	$\leqslant$6.0%

When using GYQ, a GYQ solution was made by dissolving the powder in water with a diluted solution of 0.6% and 1.2%, respectively.

- **Sika 88 L:** It is provided by Sika Sverige AB in Sweden. It is a dark brown liquid, based on vinsol resin which can be classified as natural air entraining agent. The technical data of Sika 88 L is shown in table 3.3 below:

Table 3.3 Technical data of Sika 88 L

Colour and shape	Dark brown liquid
Density	1.07 kg / dm ^{3}
pH value	approximately 13
chloride content	<0.10% by weight of the solvent
Alkaline Content, eq. Na_2O	<2.5% by weight of the solvent
Solids	About 20%
Viscosity	Light liquid

Sika 88 L used in this study was diluted to 2% solid content.

- **BASF Micro Air (called BASF thereafter):** It is provided by BASF AB in Sweden. It is based on a synthetic surfactant. The technical data of BASF is shown in table 3.4 below:

Table 3.4 Technical data of BASF

Colour and shape	Transparent liquid
Density	1.0 ± 0.01 kg/dm ^{3}
pH value	10.5-12.5
chloride content	<0.01%

Alkaline Content, eq. Na_2O	1.24%
Solids	11% ± 1%
Storage time	12 months between 5 ° C and25 ° C

BASF was used by solution in this study which was diluted to 1.1% solid content.

3.1.2 Cements

Two kinds of cements were used in the tests.

One is Swedish cement called "Anläggningscement", corresponding to CEM I 42.5 N MH/SR/LA. It has a low C_3A content and satisfies the requirements for sulfate resistance and low-alkaline cement according to EN 197-1. Its compact density is 3200 ± 20 kg/m^3 and Blain specific surface is 310 ± 30 m^2/kg.

Another is Portland Cement CEM I 42.5R which produced by Akmenés Cementas, Lithuania. Its compact density is 3140 kg/m^3, Blain specific surface is 410 ± 20 m^2/kg and equivalent alkali content is 0.92% ± 0.10%.

The size distributions of the two cements are shown in Figure 3.1.

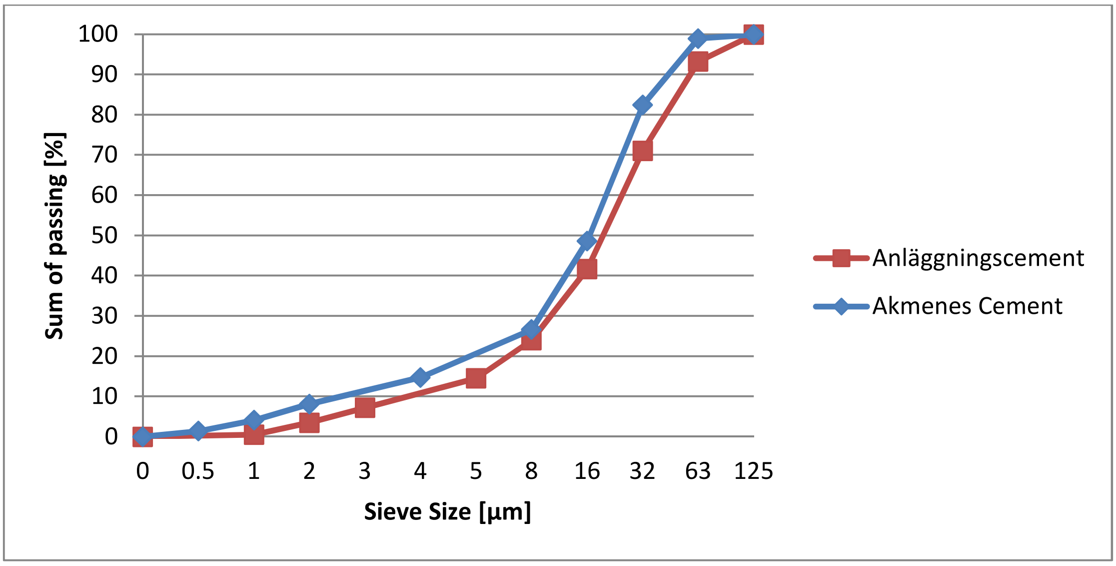

Figure 3.1 Size distribution of Anläggningscement and Akmenes cement[1]

Other technical data of these two cements are all shown in appendix A.

3.1.3 Sand

The sand used in the tests was sea-dredged sand. The maximum size of the sand is 2 mm and the size distribution is shown in table 3.5 below:

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[1] *The size distribution test is based on SS-EN 196-2*

Table 3.5 Size distribution of sea sands

Sieve size [mm]	Sum of passing [%]
2	100
1	95.3
0.5	77.5
0.25	25.5
0.125	0.7
0.063	0.2

3.2 Test procedure and equipment

In this study, all tests were conducted at the central laboratory of Thomas Concrete Group. During the whole tests the laboratory maintained a temperature of 20 ± 2°C, and the relative humidity of around 50%. The temperature of water used in mixture is potable water with a temperature of 20°C. These conditions were also kept when single or double tests were performed.

3.2.1 Mortar test

The mortar mixing procedure were conducted according to EN 196-1:2005. The total mixing time was 4 minutes within both low rotation (140 ± 5 min^{-1}) and high rotation (285 ± 10 min^{-1}). All the mortar mixed with *w/c* = 0.5, which contains 1350 g aggregates (sea-dredged sand), 500 g cement, 250 g water and a designed amount of AEA. The mixer used in the test is showed in figure 3.2.

Figure 3.2 Mixer

The test procedure used was:

- Weigh 500 g of cement and 250 g of water and put them into the bowl. Start to mix immediately when the cement is added to the water. Note the time as the mixer is started at the nearest minute ("zero time"). Let the cement and water mix for 30 seconds at low speed.

- Slowly put 1350 g aggregates in the bowl during 30 seconds (30 sec.-60 sec.).
- When all aggregate is added, raise the mixer to high speed and mix for 30 seconds (60 sec.-90 sec.).
- Stop the mixer for 90 seconds (90 sec.-180 sec.), during this period scrape down any material along the edges to the centre of the bowl and make sure the mortar is mixed evenly from top to bottom.
- Start mixer on high speed and mix for 60 seconds (180 sec.-240 sec.), then stop.

Furthermore in order to measure the stability of fresh concrete in one hour, we need to remix the mortar every 15 minutes before the measurement of air content for 10 seconds at low speed.

3.2.2 Gravimetric method

Figure 3.3 Gravimetric method

In order to measure the total air content in fresh concrete, gravimetric method was used in this study. This method employs a simple container with 404 ml volume and 87.2 g weight (see Figure 3.3). After mixing, the container was filled in three equal layers, each layer was compacted with ten strokes of the tamper, and a thin steel ruler was used to remove any excess mortar. Then the total weight $M_{measure}$ of the container and the mortar inside were recorded.

The air content (in % by volume) is calculated using the following equation:

$$V_{air} = \frac{\rho_{theoretical} - (M_{measure} - M_{container}) / V_{container} \cdot 1000}{\rho_{theoretical}} \tag{3.1}$$

Where $\rho_{theoretical}$ can be defined as:

$$\rho_{theroetical} = \frac{M_{cement} + M_{agg.} + M_{water}}{M_{cement}/\rho_{cement} + M_{agg.}/\rho_{agg.} + M_{water}/\rho_{water}} \tag{3.2}$$

Based on equations 3.1 and 3.2, the total air content can be calculated.

In this study, the air content in fresh concrete was measured by gravimetric method at every 15 minutes during one hour, i.e. at the time of 0, 15, 30, 45 and 60 minutes after stop of the mixing procedure described in 3.2.1. Before each measurement (except the first one at 0 min) the mortar was mixed for 10 seconds at low speed to simulate rotation of concrete container during transportation. In-between the measurements the fresh concrete was covered by a wet towel to protect it from drying. The AVA (see the next section) was also used, but only at time 0 and at 1 hour, to investigate the changes of the air void system along the time.

3.2.3 Air void analyzer (AVA) test

- **Equipment**

The Air Void Analyzer (AVA) is an apparatus that measures the air void characteristics of fresh concrete (see Figure 3.4). The equipment consists three main parts.

1. The sampling part consists of a wire basket, a sampling syringe and a holder that vibrates. The cage is vibrated into the concrete to extract a mortar sample of 20 cubic cm. In this study, mortar test were done so the sample could be extracted directly.
2. The sample is transferred to the base of the AVA cylinder, and placed into the analysis liquid.
3. The data analysis tool controls and monitors the test and computes the air content in the paste, the specific surface of the air voids, and the spacing factor of the air void structure.

Figure 3.4 The Air Void Analyzer

The measured three parameters air content, specific surface and spacing factor describes the characteristics of an air void system. By using AVA, it is possible to assess the air void characteristics of the concrete when it is fresh. This makes it possible to modify the concrete mixture directly if required. One more advantage of AVA is that the equipment is portable so it is applicable for in-situ measurements.

- **Test procedure**

A 20 ml mortar sample was extracted from the mortar in the container used for determining the entrained air content by the gravimetric method as described in 3.2 (Figure 3.5). The sample was placed into the equipment for measurement. The components of the AVA equipment are illustrated in Figure 3.6:

Figure 3.5 Taking the sample

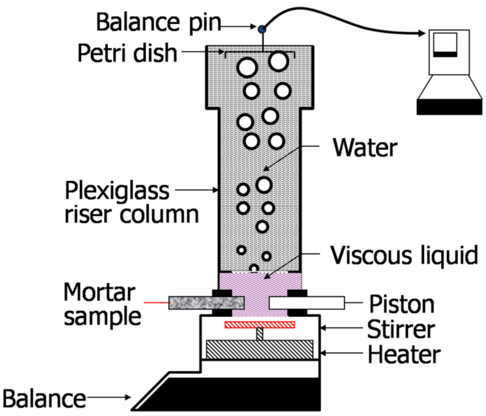

Figure 3.6 Components of AVA

The mortar sample was injected into the viscous liquid and they were stirred together. The air bubbles within the mortar paste are released and start to rise. According to Stoke's law, the big air bubbles rise faster than the small ones. Based on the amount of bubbles, the speed of the rising bubbles was registered by a balance and the computer, which linked with the equipment, can calculate the air content, spacing factor, specific surface area and air size distribution in the mortar sample.

In this method, large air bubbles like the entrapped air was omitted, as the equipment is only able to measure air bubbles less than 2 mm in diameter.

The AVA works in the procedures as described below:

- The AVA riser column, Plexiglas, is filled at its base with a viscous (glycerine based) liquid and topped with water.
- The mortar is injected into the viscous liquid and stirred for 30 seconds to release the air bubbles.
- The air bubbles rise and are collected at the top of the water column beneath the inverted petri dish.
- The inverted dish is attached to a sensitive balance. A change in its mass caused by the buoyancy of the air bubbles is recorded by the computer for 25 minutes.
- This allows the computation of the air void parameters. Air voids greater than 2 mm are excluded from calculations.

4 Result and Analysis

4.1 Effect of different kinds of AEAs

In the first step of the test, the aim was to compare four available AEAs for their air entraining compatibility, the air void system and the air stability. In order to compare them more easily, the dosages of the AEAs were based on the diluted AEA solutions, that is, by weight percentage of solid, 0.45% Sika-S solution, 0.6% and 1.2% GYQ solution, 2% Sika88 L solution and 1.2% BASF solution were used in the test.

In order to make it simpler, when it comes to normal air content, a dosage of around 0.3% of the diluted solution by weight of cement was taken for all the AEAs; when it comes to maximum air content, the dosage over 3% of the diluted solution by weight of cement was taken for all the AEAs. The actual dosage of, for example, Sika-S at normal air content was then 0.00135% (0.3% × 0.45%) by weight of cement.

4.1.1 Comparison of air content

Normally, around 4.5% to 5.5% air content is required in concrete for freeze-thaw resistance in Sweden. However, in mortar only fine aggregates are used, because of the absent of coarse aggregates the air content in mortar is nearly twice of that in concrete at the same condition. Hence, in the mortar test air content of about 11% was aimed at as the normal condition. After trial and error tests, it was concluded that at a dosage around 0.3% by weight of cement all of these four AEAs can entrain a total air content of around 11% (Table 4.1)

Table 4.1 Air content at a normal dosage

AEA	Dosage [% of Cem in solution](Actually)	Air content [%]
GYQ (0.6% solution)	0.3 (0.0018)	11.3
Sika-S (0.45% solution)	0.3 (0.00135)	11.3
Sika 88 L (2% solution)	0.2 (0.004)	11.8
BASF (1.1% solution)	0.3 (0.0033)	11.5

The normal dosage and normal air content are useful for practical usage. The table above can provide guidance on which dosage gives the normal air content. However, for the research purpose it is interesting to also find the dosage for the maximum air content. In Table 4.2 the maximum air content of these four kinds of AEAs is presented:

Table 4.2 Maximum air content

AEA	Dosage [% of Cem. in solution](Actually)]	Air content [%]
GYQ (1.2% solution)	3.9 (0.0468)	25.3
Sika-S (0.45% solution)	5.4 (0.0243)	32.1
Sika 88 L (2% solution)	3.9 (0.078)	30.6
BASF (1.1% solution)	4.0 (0.044)	21.4

4.1.2 Comparison of stability

It is not enough to make a conclusion of which is the best AEA by only compare their ability to entrain air. So tests on stability of the entrained air in fresh concrete were taken as a part of the whole test program.

For the dosage of around 0.3% of the cement which leads the entrained air around 11%, the stability of entrained air was tested for every 15minutes during one hour. Figure 4.1 shows the stability of the air void system during one hour and the data are all shown in Table B.9 in appendix B:

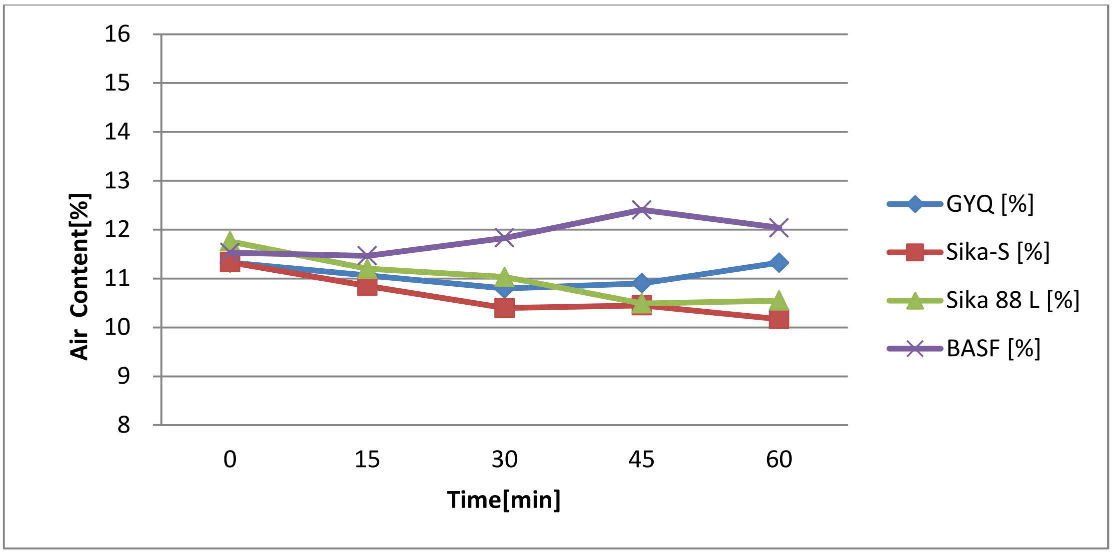

Figure 4.1 Stability of air in fresh mortar at a normal dosage (around 0.3% Cem.)

We can see from Figure 4.1 that for most of the AEAs the air content slightly decreases with time. However, for BASF, the air content increases with the time. Also we can conclude from the figure that GYQ has more stable air at the normal dosage than the others during one hour while Sika 88 L changes the most in this one hour.

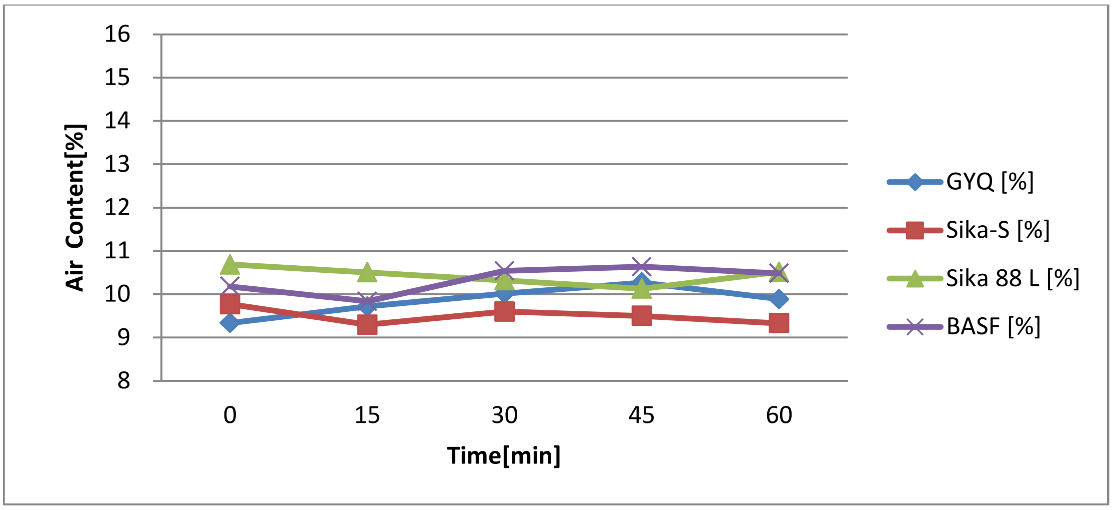

Figure 4.2 Stability of air in fresh mortar at a dosage of 0.15% Cem.

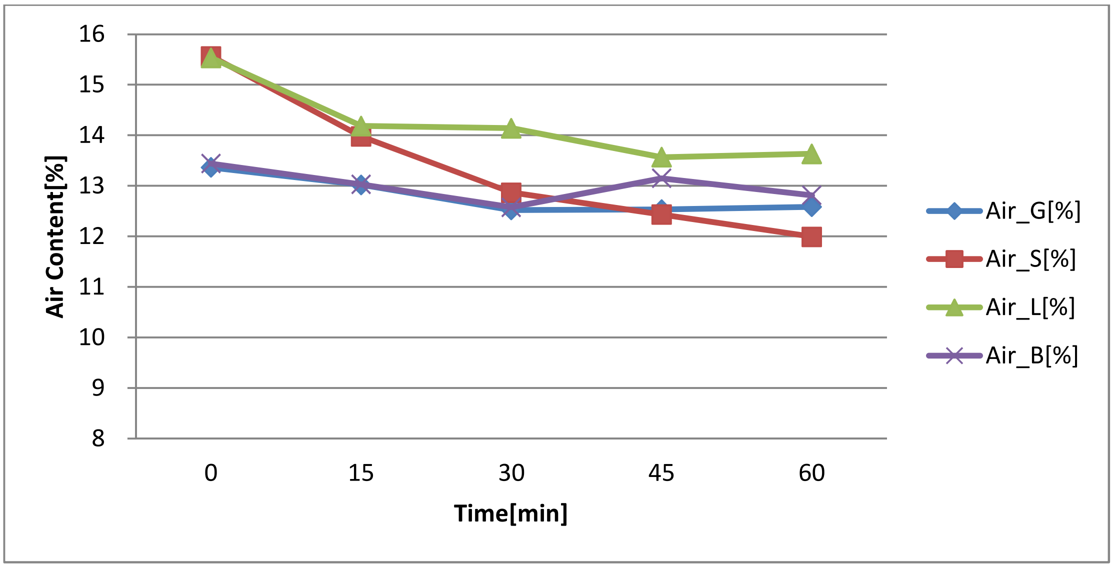

Figure 4.3 Stability of air in fresh mortar at a dosage of 0.45% Cem.

The air content results at the dosage 0.15% of Cem and 0.45% of Cem are shown in Figures 4.2 and 4.3. It can be seen that at the low dosage (0.15% Cem), all four AEAs functioned similarly with regard to both air content and stability. At a higher dosage (0.45% of Cem), both GYQ and BASF behavior relatively stable, while the AEAs from Sika gave markedly higher initial air content but decreased with time, especially Sika-S.

When it comes to the maximum air content, based on the certain dosages for reaching the maximum air contents, air stability tests were also made to see which AEA keeps the air system best in fresh concrete along with time and which is the worst. The results of the tests shown in Figure 4.4 below (Table B.10 shows the data in this figure):

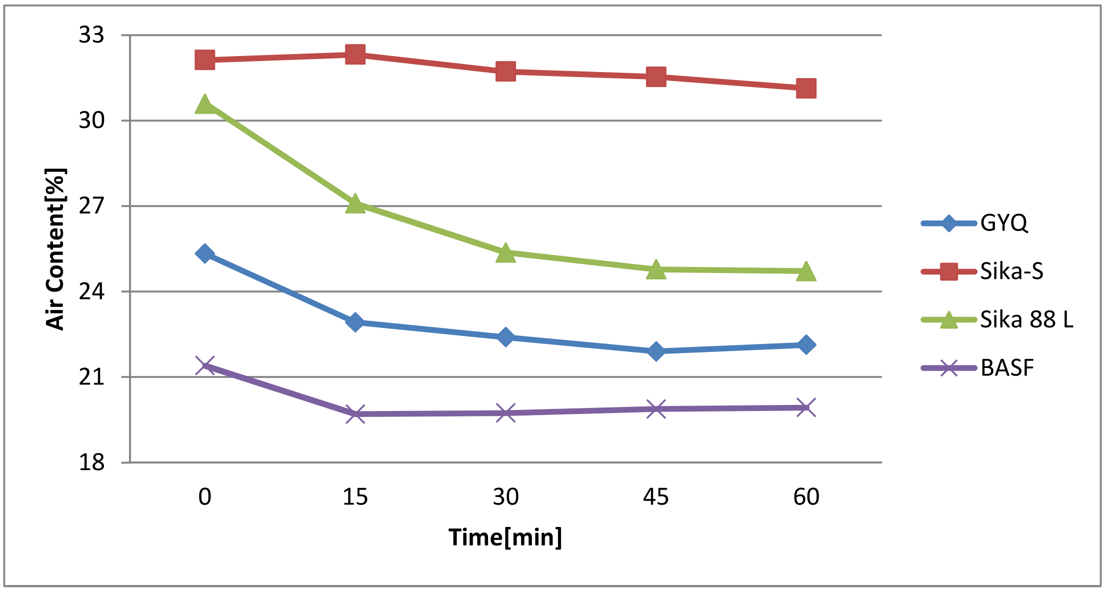

Figure 4.4 Stability of maximum air content in fresh mortar

From this figure it is clear that Sika-S and Sika 88 L can produce higher air content at first. But Sika 88 L was very unstable and the air content decreased from 30.6% to 24.7% during one hour. The BASF AEA produced the smallest air content but with a very stable air void system. At the same time, GYQ was in the middle in both air content and stability of air. It is important to note that in Figure 4.4 the Sika-S revealed the best stability at the high dosage (5.4% Cem in this study, see Table 4.4), different behaviour when used at the normal dosage (≤ 0.45% Cem, see Figures 4.1 to 4.3).

4.1.3 Comparison by AVA

- **Basic data from AVA**

Since a test of AVA takes 40 minutes, measurements by AVA were carried out immediately and one hour after mixing. Because of the uncertainty of the measurements, for every dosage the measurements by AVA were repeated at least twice. The details are shown in appendix B, and summarized in Tables 4.3 and 4.4.

Table 4.3 Data of air void system from AVA immediately after mixing

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	0.3%C	16.5	11.1	39.5	0.06
Sika-S	0.3%C	16.7	10.5	33.6	0.07
Sika88L	0.2%C	16.3	11.3	41.2	0.05
BASF	0.3%C	16.0	12.6	45	0.05

Table 4.4 Data of air void system from AVA one hour after mixing

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface Area [mm^{-1}]	Spacing factor [mm]
GYQ	0.3%C	17.7	12.5	38.2	0.06
Sika-S	0.3%C	18.8	12.4	37.9	0.05
Sika88L	0.2%C	19.8	14.3	38.2	0.05
BASF	0.3%C	12.8	10.5	39.5	0.08

*Table 4.5 Air content measured by gravimetric method on the same sample**

AEA	Dosage	Air content (Immediately) [%] (Stdev.)	Air content (One hour) [%] (Stdev.)
GYQ	0.3%C	11.7 (0.05)	11.5 (0.06)
Sika-S	0.3%C	12.6 (0.89)	12.0 (0.69)
Sika88L	0.2%C	11.8 (0.59)	11.7 (0.18)
BASF	0.3%C	11.5 (0.37)	12.2 (0.09)

* Average values from two measurements.

From the tables above, it is obvious that for the first three AEAs the air content increased while BASF decreased after one hour measured by AVA. And so does the specific surface area and spacing factor, which improved or was stable for GYQ, Sika-S and Sika 88 L but became worse for BASF.

By using the AVA, two important data (specific surface areas and spacing factor) can be measured. Specific surface area is the total surface areas per unit bulk volume. It is defined as the surface area divided by volume (mm^2/mm^3). The spacing factor is average maximum distance in the cement paste from the periphery of a void. These two data show the properties of the entrained air in the concrete and are affected by both air bubble size and total air content. It is obvious that a large specific surface area implies either large air content or large amount of small air bubbles.. However, it is not enough to study the air void system by only these two characteristics. Air size distribution will be shown later to make comparison and discussion.

Also from table 4.5 we can see that although all of the AEAs showed good abilities on stabilizing the air bubbles, Sika-S and Sika 88 L are more sensitive to the mixing which were displayed by their larger standard deviation.

By comparing table 4.5 with tables 4.3 and 4.4, we can see that there is a difference in air content as measured by AVA and the gravimetric method (GM). The relationship between air contents measured by AVA and GM is shown in appendix B. In this comparison there are 32 groups, but two results by GM deviate significantly from the

AVA and have been deemed to be outliers. Hence, the results from AVA with different air size (2 mm, 0.35 mm) are compared with GM, based on least squares fitting, as shown in Figures 4.5 and 4.6.

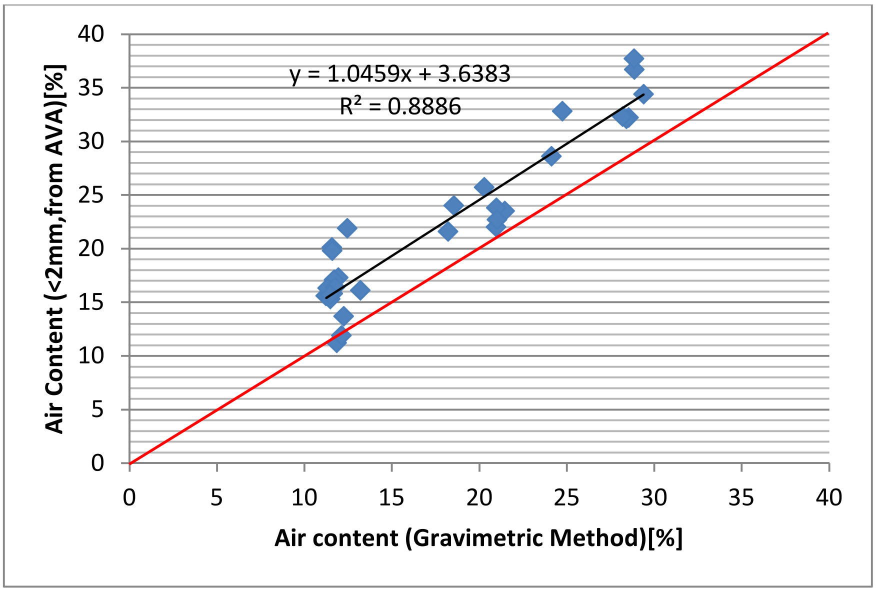

Figure 4.5 Comparison of air content measured by GM and AVA (2 mm)

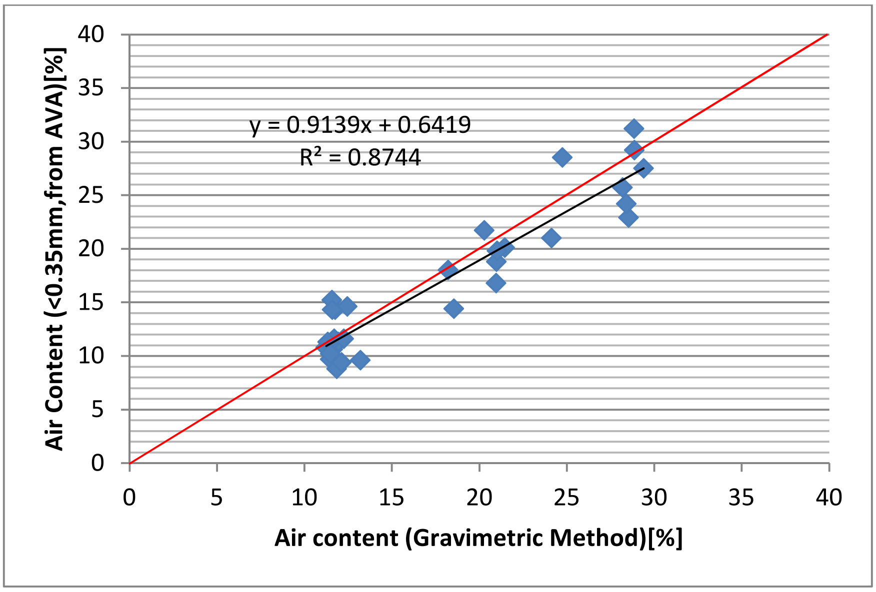

Figure 4.6 Comparison of air content measured by GM and AVA (0.35 mm)

It can be seen from Figure 4.5 that the air content measured by GM is generally lower than that measured by AVA when comparing for air bubbles up to 2 mm. When comparing GM gravimetric method with AVA for air bubbles up to 0.35 mm, Figure 4.6, it can be seen that the air content measured by GM is slightly higher than AVA (0.35 mm). The above two comparisons indicate that the GM approach is closer to AVA for air bubbles up to 0.35 mm with less bias.

One possible reason for the deviation could be that the sampling for the AVA is from the upper portion of the cylinder, which may contain more air, especially large bubbles, due to compaction and the buoyancy effect, resulting in a higher air content than the average as measured by the GM.

- **Air size distribution**

The AVA can record the size distribution of the air bubbles and presents the data for a certain air bubble size as percentage of the total air content. The size of the air bubbles vary between 0 and 2 mm.

Figures 4.7 and 4.8 below show the size distribution of the air bubbles in mortar sample. As it is known, the most efficient air sizes with respect to the frost resistance are those below 300 μm. From the size distribution graphs, it is clear that BASF can produce the most efficient air among the four AEAs. Although Sika-S can produce the most air bubbles, its air size distribution (high amount of the large bubbles) is not as good as the others.

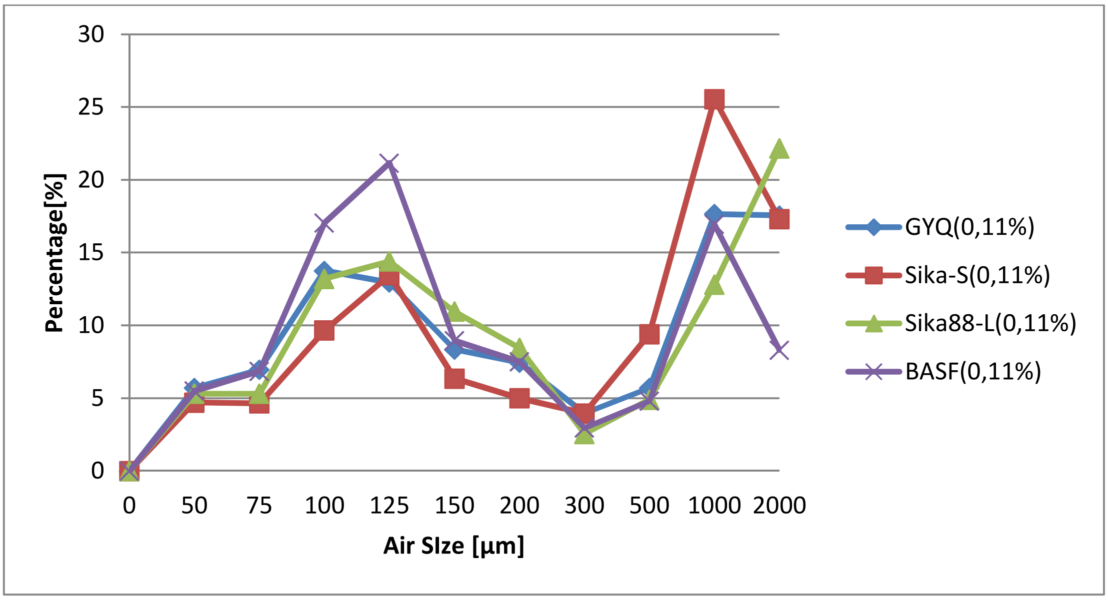

Figure 4.7 Size distribution of air in mortar sample (at a normal dosage, immediately)

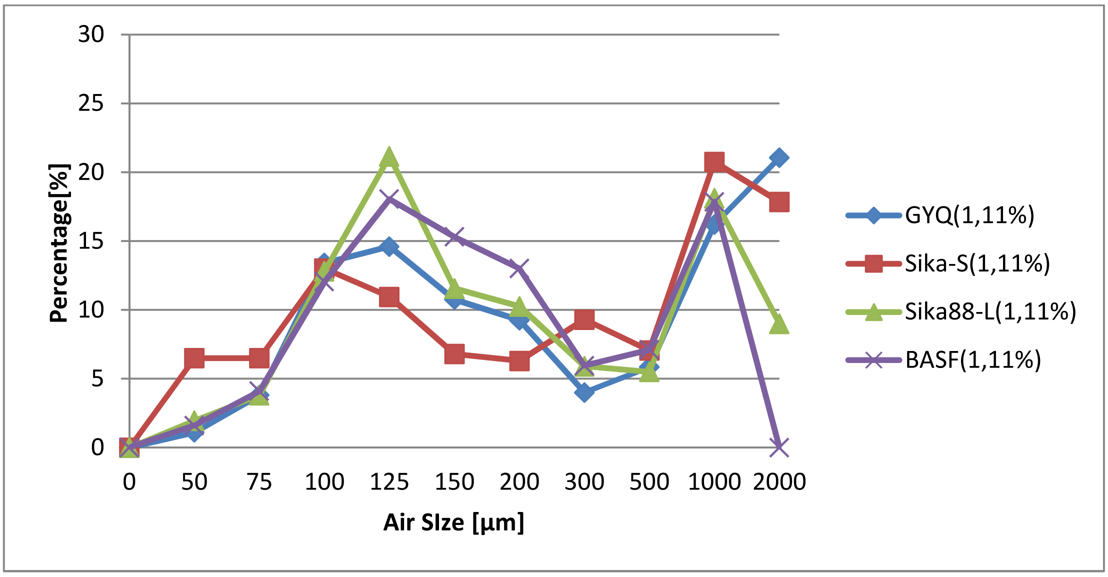

Figure 4.8 Size distribution of air in fresh concrete (at a normal dosage, one hour later)

Since the total air contents of all the AEAs in the sample are not the same it is difficult to compare them only based on the size distribution. Therefore the air volume for each bubble size in the 20ml mortar sample was calculated. The result is shown in Figures 4.9 to 4.12. The comparisons on the maximum air content are shown in Figures 4.13 to 4.16.

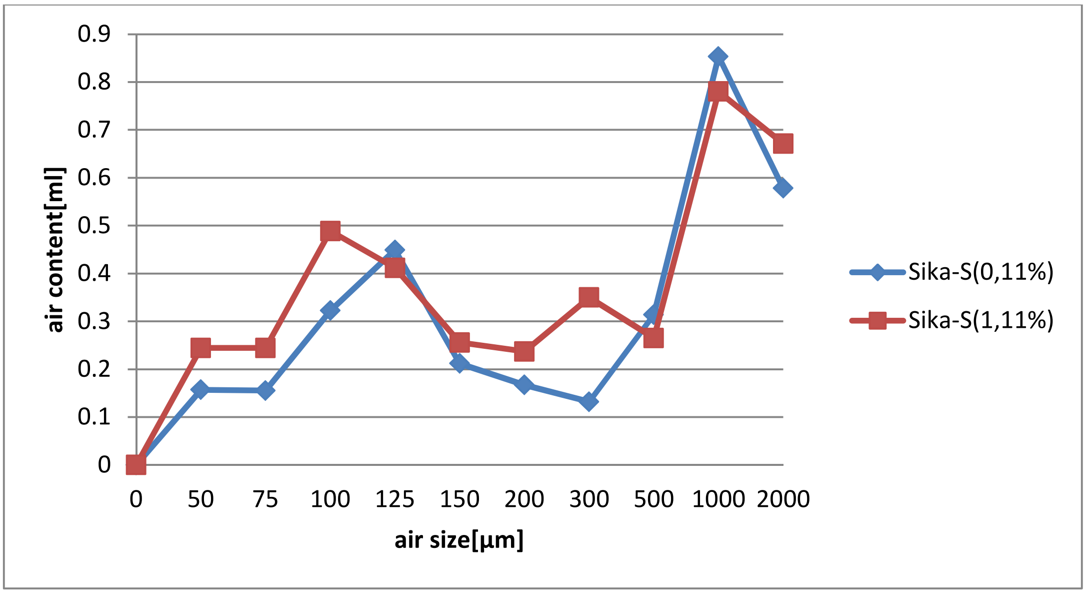

Figure 4.9 Size distribution for Sika-S in real volume[2]

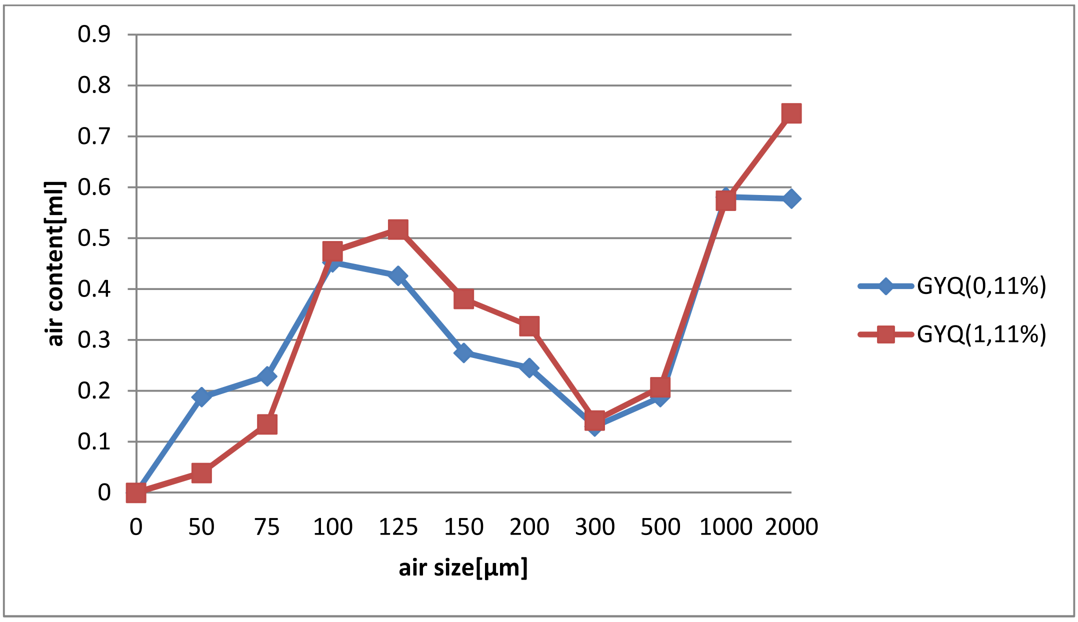

Figure 4.10 Size distribution for GYQ in real volume

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[2] 0 represents for measured immediately and 1 represents for measured on hour later.

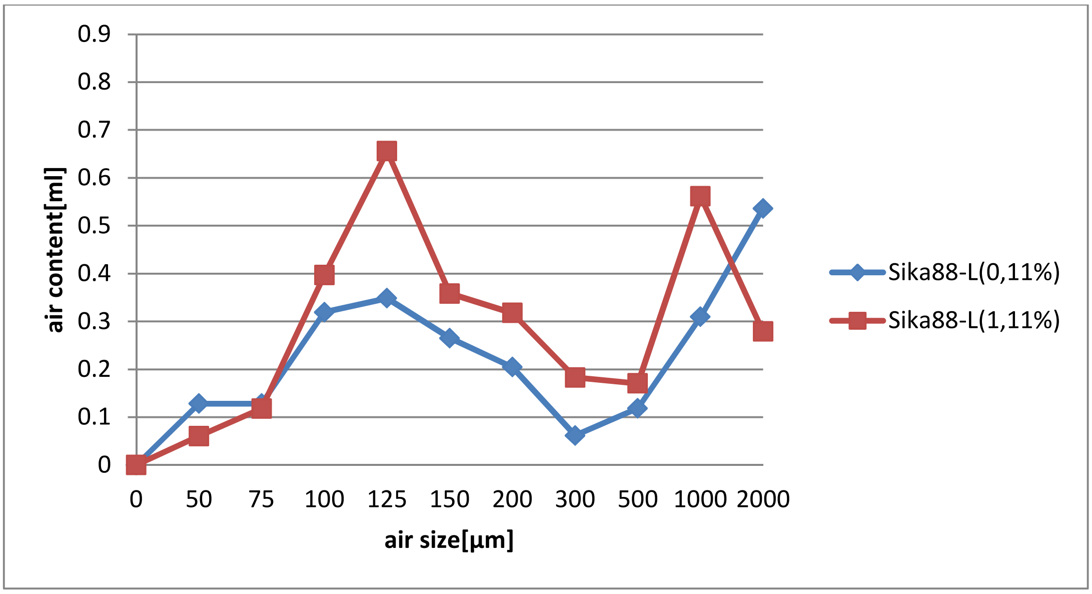

Figure 4.11 Size distribution for Sika 88 L in real volume

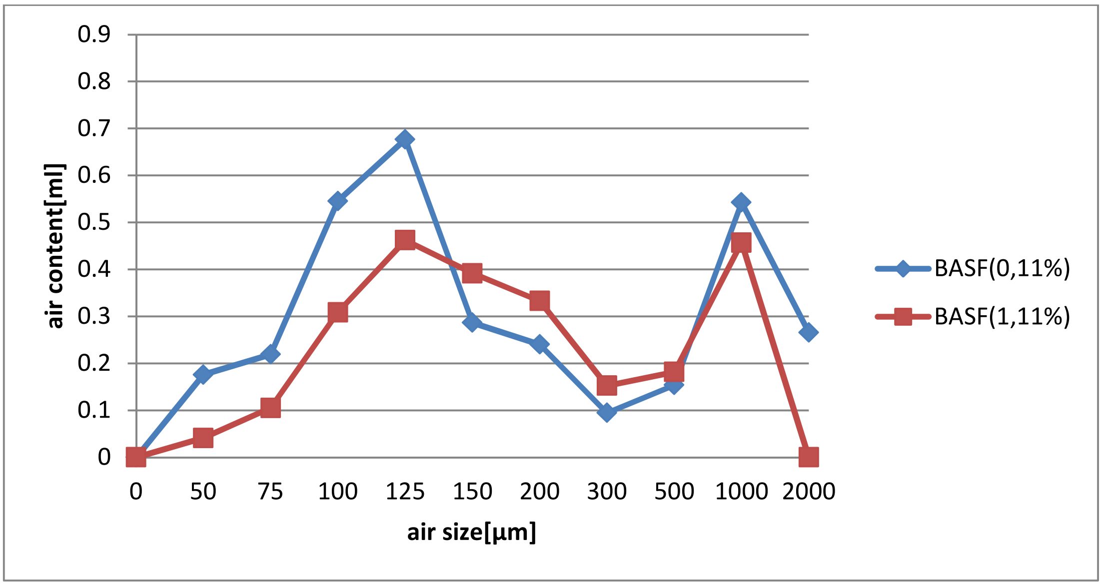

Figure 4.12 Size distribution for BASF in real volume

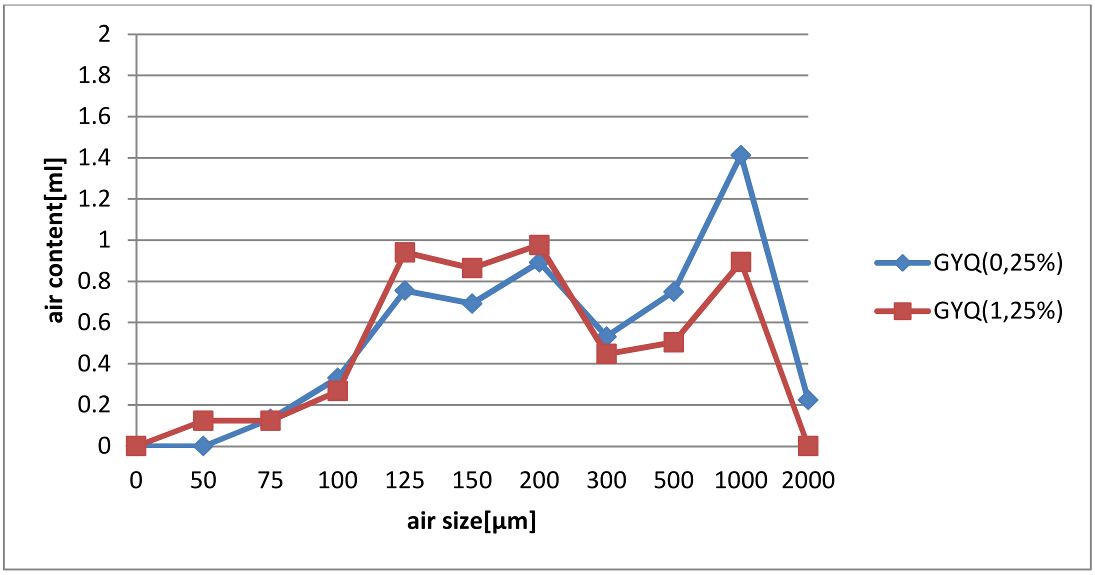

Figure 4.13 Size distribution for GYQ in real volume

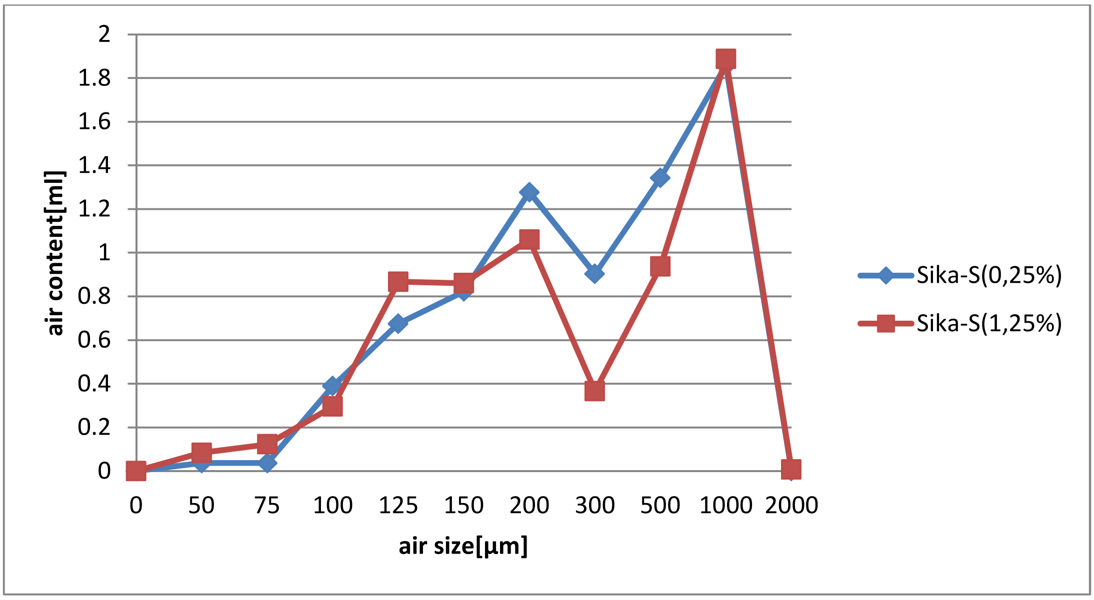

Figure 4.14 Size distribution for Sika-S in real volume

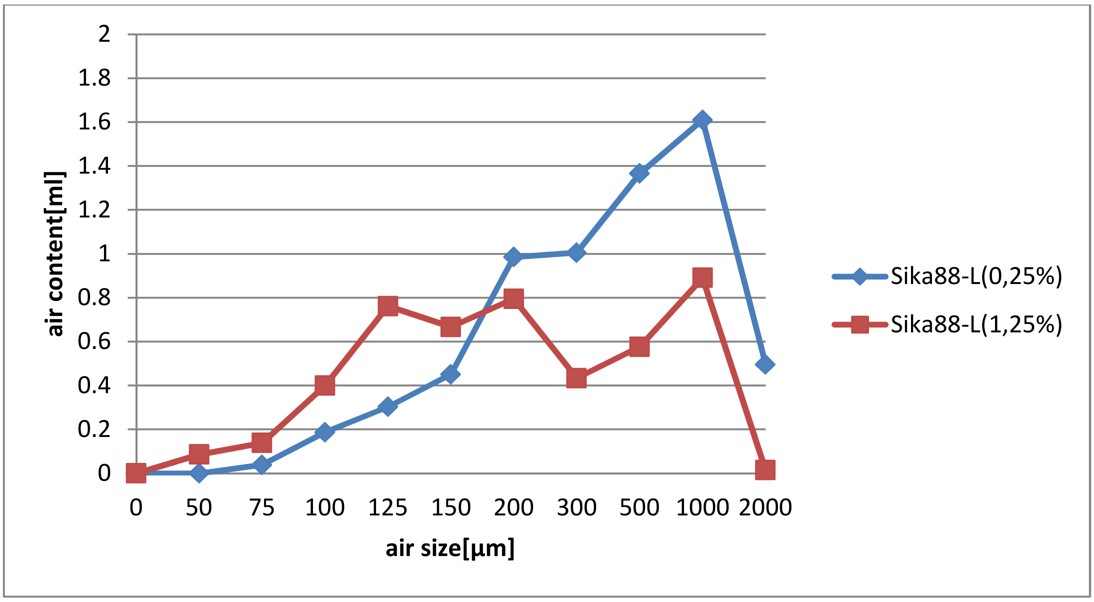

Figure 4.15 Size distribution for Sika 88 L in real volume

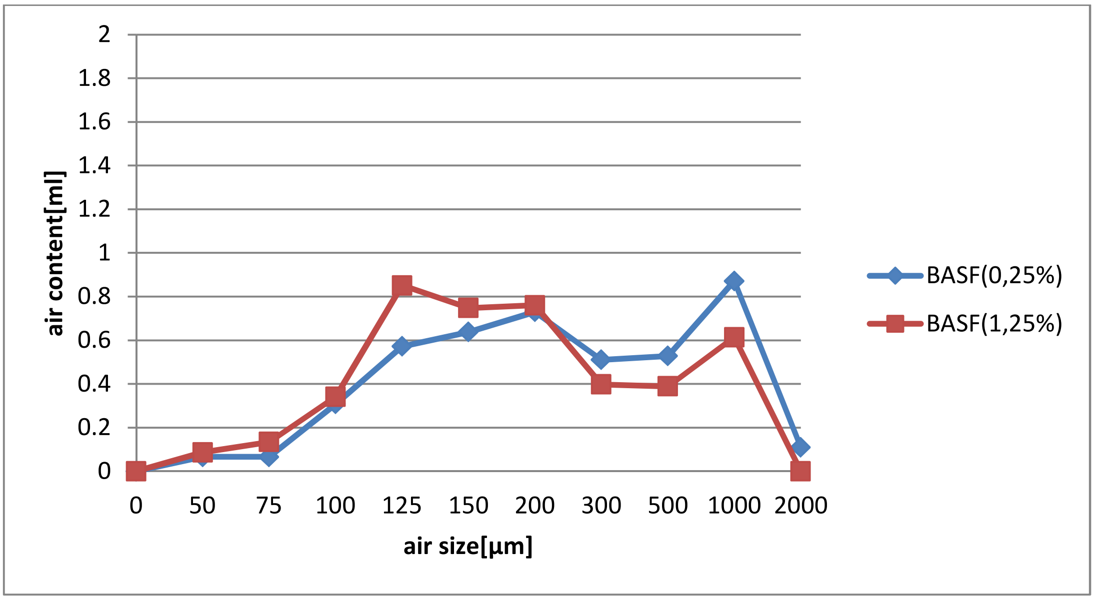

Figure 4.16 Size distribution for BASF in real volume

From the results of the normal dosage, the volume of efficient air increased after one hour with Sika-S and Sika 88 L, while with BASF it decreased. For GYQ the volume of air bubbles with the size between 0 and 100 µ m decreased and those with the size between 100 µ m and 300 µ m increased. When compare with AEAs the total air volume of Sika-S (3.34 ml) is slightly larger than GYQ (3.29 ml), but the volume of efficient air is smaller than that of GYQ. For Sika 88 L, although the volume of air bubbles with the size around 125 µm increased a lot after one hour, for the volume of big air bubbles also increased. It is noticed that the total air volume of Sika 88 L increased a lot after one hour (from 2.42 ml to 3.1 ml), which is an indication of instability. For BASF, the efficient air decreased after one hour.

From the results of the maximum air content shown in Figures 4.13 to 4.16 it can be seen that the efficient air volume after one hour in general became better for all types of AEAs. It should be noted that the mortar was mixed again for 10 seconds after one hour before sampling for AVA test. The improved pore size distributions may be attributed to the increase in viscosity of the paste one hour after initial mixing. This increased viscosity helps to keep the small size air bubbles in the paste.

Moreover, from Tables 4.6 and 4.7 it can be conclude that for all AEAs the total air content decreased after one hour, which was just like the measurements from GM while for GYQ and BASF the efficient air content were slightly increased. For all AEAs the specific surface area increased after one hour and the spacing factors were stable.

Table 4.6 Data of air void system from AVA immediately (maximum air content)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	28.6	21	29.3	0.04
Sika-S	3%C	36.7	29.2	29.2	0.03
Sika88L	3%C	32.2	22.9	23.5	0.04
BASF	3%C	22	16.8	32.1	0.04

Table 4.7 Data of air void system from AVA one hour later (maximum air content)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	25.7	21.7	37.3	0.03
Sika-S	3%C	32.1	24.2	30.8	0.03
Sika88L	3%C	23.8	18.8	34.9	0.04
BASF	3%C	21.6	18	37.9	0.04

From Figures B.9 and B.10 it can be seen that Sika 88 L produced the least efficient air among these four AEAs while BASF produce the most.

One thing that should be noted is that, although Sika-S produced the most air bubbles at the maximum air content, its efficient air after one hour was the smallest, of the total air a large part of the air bubbles were with large sizes. However, this may be an effect of the extremely high air content which can affect the stability negatively.

4.2 Effect of AEAs in Different Cementitious Materials

In order to study the properties of the AEAs more deeply, in the second step Sika-S and GYQ were chosen for further study. They were chosen as Sika-S is a synthetic AEA which can produce the most air bubbles in concrete among these four while GYQ is the one based on natural material which can produce better air void system with relatively good stability. In the following tests diluted 1.2% GYQ solutions and 0.45% Sika-S solutions were used.

In the first part, all the cement used for the test was Anläggningscement, in the second stage another cement with a higher fineness and alkali, Akmenes cement, was used. In addition, Akmenes cement with slag was also investigated, both for the tests in the fresh mortar with the maximum air content (dosage about 3% by weight of cement). The air was evaluated by both the gravimetric method and the AVA.

4.2.1 Akmenes cement

By just changing the cement from Anläggningscement to Akmenes cement, the same tests as previously used were carried out in the fresh mortar with the maximum air content. Table 4.8 shows the stability of air void system measured by gravimetric method during one hour. Tables 4.9 and 4.10 show the data measured by AVA. The results are discussed in section 4.2.3.

Table 4.8 Stability of air in fresh mortar (Akmenes cement)

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	3%C	22.9	21.6	20.7	19.9	19.9
Sika-S	3%C	29.6	28.9	28.2	27.8	27.5

Table 4.9 Data of air void system from AVA immediately (Akmenes cement)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	32.8	28.5	37.3	0.03
Sika-S	3%C	34.4	27.5	21.2	0.04

Table 4.10 Data of air void system from AVA one hour later (Akmenes cement)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	22.7	19.8	35.7	0.04
Sika-S	3%C	32.3	25.7	26.7	0.04

Here all GYQ solutions are 1.2% of solid and all Sika-S solutions are 0.45% of solid.

4.2.2 Akmenes cement with slag

The slag used in the test is Slag Bremen which has a compact density of 2900 kg/m^3, compared with the cement which has about 3100 kg/m^3. In this study 1/3 of cement by weight was replaced by slag. The dosages of all the components used in the tests were shown in Table 4.11 below:

Table 4.11 Dosages of components

Component	Dosage [g]	Density [kg/m^3]
Water	250	1000
Akmenes cement	335	3140
Slag	165	2900
Aggregate	1350	2650

Table 4.12 shows the stability of air void system in the mortar with slag measured by gravimetric method during one hour. Table 4.13 and 4.14 show the data measured by AVA.

Table 4.12 Stability of air in fresh mortar (Akmenes cement with slag)

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	3%C	19.1	18.3	17.7	17.5	17.5
Sika-S	3%C	28.4	28.0	27.7	27.3	27.0

Table 4.13 Data of air void system from AVA immediately (Akmenes cement with slag)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	23.5	20.1	34.6	0.04
Sika-S	3%C	37.7	31.2	31.6	0.03

Table 4.14 Data of air void system from AVA one hour later (Akmenes cement with slag)

AEA	Dosage	Air content (<2 mm) [%]	Air content (<0.35 mm) [%]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ	3%C	24	14.4	23.8	0.06
Sika-S	3%C	47.5	31.2	22.9	0.03

Here all GYQ solutions are 1.2% solid content, and all Sika-S solutions are 0.45% solid content.

4.2.3 Comparison of Anläggningscement, Akmenes cement and Akmenes cement with slag

The air content and its relative changes with time are shown in Figure 4.17. When comparing the stability of air in fresh mortar between Akmenes cement and Akmenes cement with slag the following conclusions/observations can be made:

1) Sika-S is always more stable than GYQ regardless of the kinds of cementitious materials. This is probably due to the difference between synthetic and natural air entrainers.
2) The stability of air was improved by replacing 1/3 Akmenes cement with slag, for both GYQ and Sika-S. This is probably because the particles of slag are finer than cement. Replacing cement with slag is kind of improving the fineness of the cementitious materials used in the test which stabilizes the air bubbles better. Another possible reason is that by adding slag the alkali of the cementitious material in the test decreased. Since the alkali environment can affect protective shell of the air bubbles and then the damaged bubbles may coalescence and become a larger one. The mortar sample with slag (lower alkaline content than only Akmenes cement) can then produce a more stable air in concrete. This may also explain why Anläggningscement (low alkali content) can produce more stable air than Akmenes cement (normal alkali content).

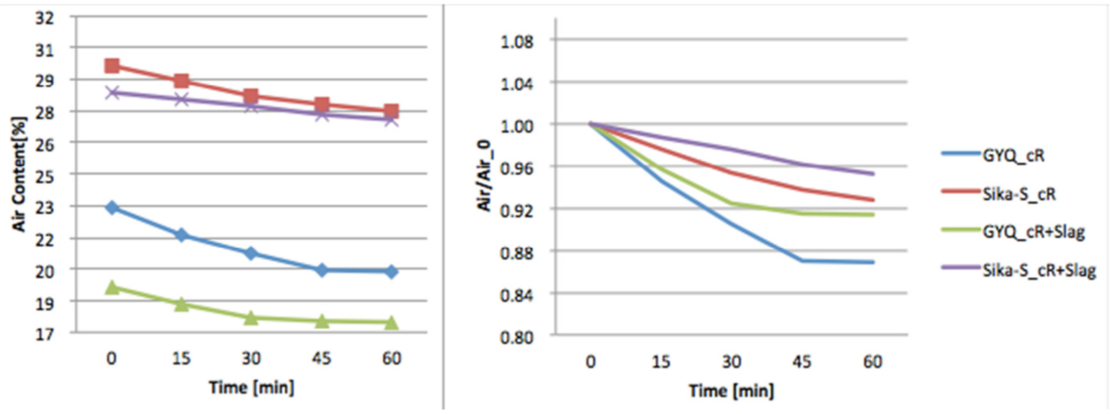

Figure 4.17 Comparison of stability of air in fresh concrete between Akmenes cement and Akmenes cement with slag

Tables 4.15 and 4.16 show the changes in air content with the different cementitious materials and air entrainers. Here it can be conclude that: Akmenes cement always contains a little more entrained air than Anläggningscement; and when replacing 33% Akmenes cement with slag, the air content decreased. However, these are only total air contents. When examining the air void system, GYQ had a decreasing air content and specific surface and the spacing factor decreased when slag was added. Also with Sika-S the specific surface decreased.

Table 4.15 Comparison of air contents with three kinds of cementitious material (measured immediately)

Category	Air content [%]	Air volume [mm^3]	Specific surface area [mm^{-1}]	Spacing factor [mm]
GYQ(CEM I 42,5N) [3]	24.14	4.83	29.3	0.04
GYQ(CEM I 42,5R) [4]	24.75	4.95	37.3	0.03
GYQ(CEM I 42,5R+33%Slag) [5]	19.14	3.83	34.6	0.04
Sika-S(CEM I 42,5N)	28.88	5.78	29.2	0.03
Sika-S(CEM I 42,5R)	29.40	5.88	21.2	0.04
Sika-S(CEM I 42,5R+33%Slag)	28.39	5.68	31.6	0.03

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[3] CEM Ⅰ 42,5N refers to Anläggningscement

[4] CEM Ⅰ 42,5R refers to Akmenes cement

[5] CEM Ⅰ 42,5R+33%Slag refers to 335g Akmenes cement and 165g slag

Table 4.16 Comparison of air contents with three kinds of cementitious material (measured one hour later)

Category	Air content[%]	Air volume [mm^3]	Specific surface Area [mm^{-1}]	Spacing factor [mm]
GYQ(CEM I 42,5N)	20.29	4.06	37.3	0.03
GYQ(CEM I 42,5R)	21.03	4.21	35.7	0.04
GYQ(CEM I 42,5R+33%Slag)	17.5	3.5	23.8	0.06
Sika-S(CEM I 42,5N)	28.41	5.68	30.8	0.03
Sika-S(CEM I 42,5R)	28.19	5.64	26.7	0.04
Sika-S(CEM I 42,5R+33%Slag)	27.04	5.41	22.9	0.03

Figures 4.18 to 4.21 below show the air size distribution in real volume for three kinds of cementitious materials: Anläggningscement, Akmenes cement and Akmenes cement with slag. In the pictures "cN" refers to Anläggningscement, "cR" refers to Akmenes cement, "cR+s" refers to Akmenes cement with slag, "0" refers to measured immediately and "1" refers to measured one hour later.

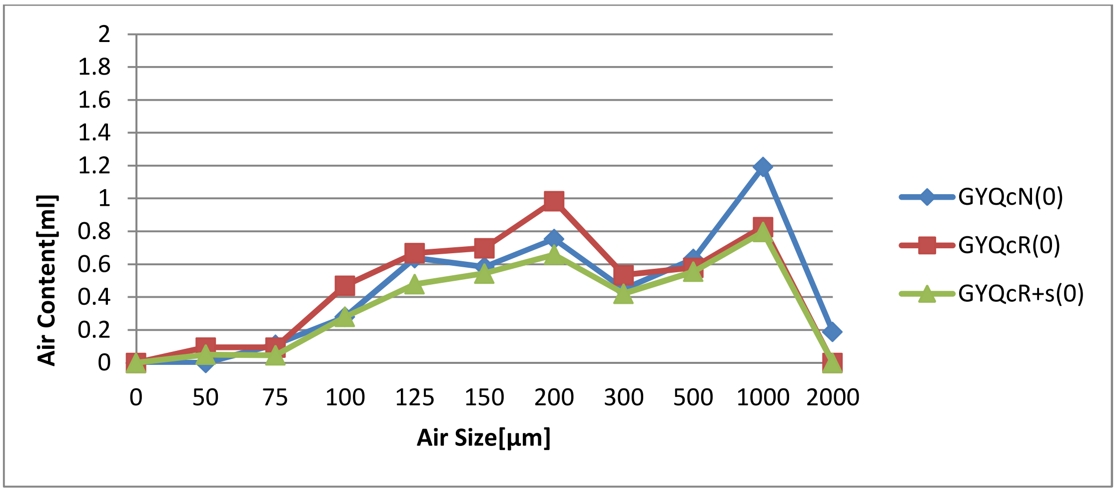

Figure 4.18 Air distribution based on real volume measured immediately (GYQ)

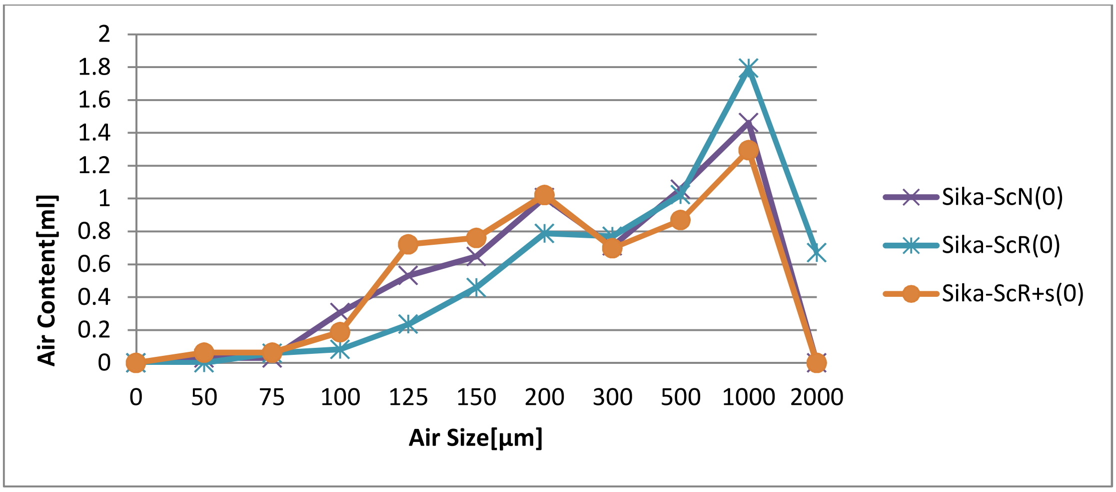

Figure 4.19 Air distribution based on real volume measured immediately (Sika-S)

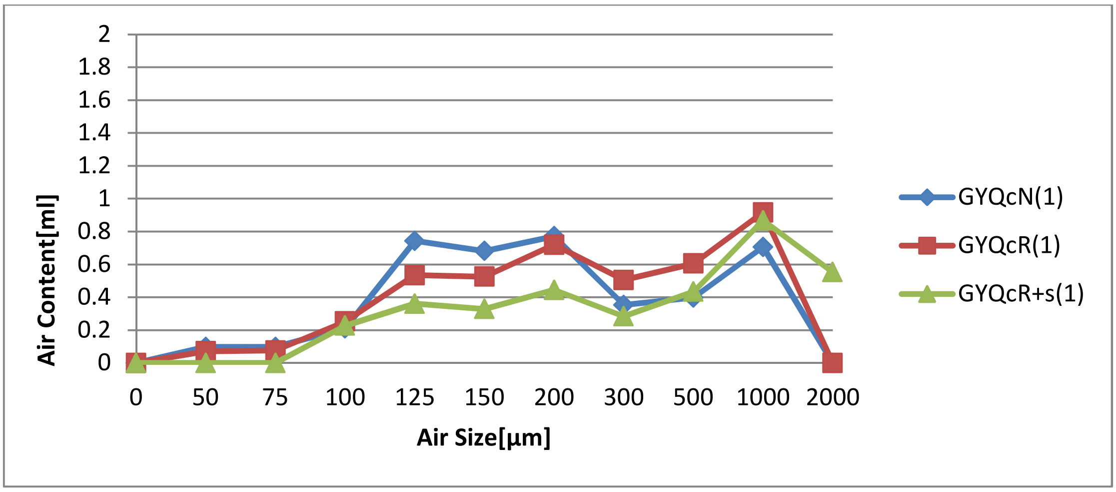

Figure 4.20 Air distribution based on real volume measured one hour later (GYQ)

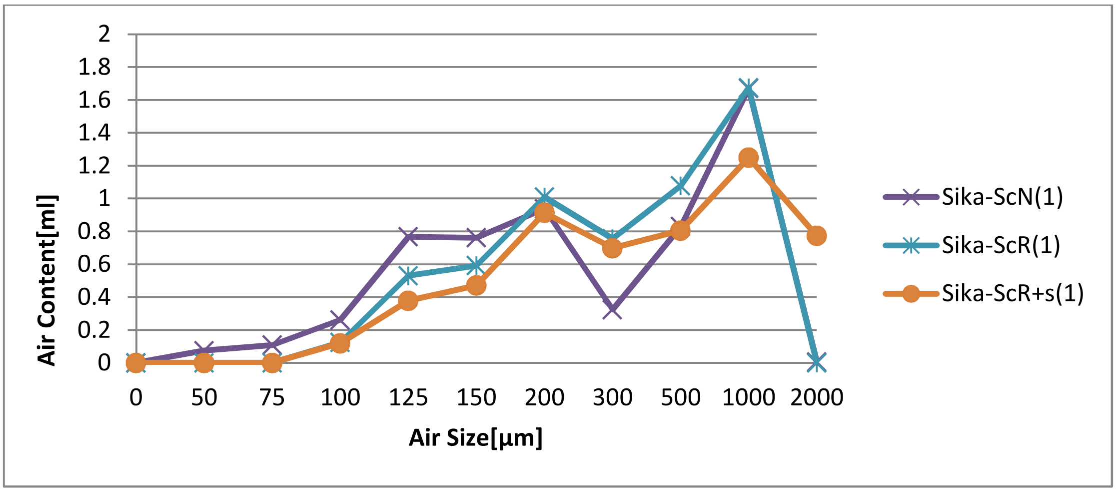

Figure 4.21 Air distribution based on real volume measured one hour later (Sika-S)

Tables 4.17 and 4.18 summarize how the air void system changed during one hour for the different cementitious materials with different AEAs, including the change of total air content and also the changes of air content in small air bubbles.

Table 4.17 Changes of air void system during one hour for all kinds of AEAs at normal air content

AEAs	Total air content by GM [%]	Change measured by AVA (air_t_{60}/air_t_0)			
		Total change air content	Change air content (< 0.35 mm)	Change air content (< 0.15 mm)	Change spec. surface
GYQ	11.7	↑	→	↓	→
Sika-S	12.6	↑ ↑	↑ ↑	↑ ↑	↑ ↑
Sika 88 L	11.8	↑ ↑	↑ ↑	↑ ↑	↑ ↑
BASF	11.5	↓ ↓	↓ ↓	↓ ↓	↓ ↓

Table 4.18 Changes of air void system during one hour for three kinds of cementitious material and two kinds of AEAs

AEAs	Cementitious materials	Total air content by GM [%]	Change measured by AVA (air_t_{60}/air_t_0)			
			Total change air content	Change air content (< 0.35 mm)	Change air content (< 0.15 mm)	Change spec. surface
GYQ	CEM Ⅰ 42,5N	24.14	↓	↑ ↑	↑ ↑	↑ ↑
	CEM Ⅰ 42,5R	24.75	↓ ↓	↓ ↓	↓ ↓	→
	CEM Ⅰ 42,5R+33%Slag	19.14	→	↓ ↓	↓ ↓	↓ ↓
Sika-S	CEM Ⅰ 42,5N	28.88	↓ ↓	↓ ↓	↑ ↑	→
	CEM Ⅰ 42,5R	29.4	↓	↓	→	↑ ↑
	CEM Ⅰ 42,5R+33%Slag	28.39	↑ ↑	→	↓ ↓	↓ ↓

The arrows indicate the change:
→ means stable ($0.95 \leq air\_t_{60}/air\_t_0 \leq 1.05$)
↓ means decreases ($0.9 \leq air\_t_{60}/air\_t_0 < 0.95$)
↓ ↓ means large decreases ($air\_t_{60}/air\_t_0 < 0.9$)
↑ means increase ($1.05 < air\_t_{60}/air\_t_0 \leq 1.1$)
↑ ↑ means large increases ($air\_t_{60}/air\_t_0 > 1.1$)

From Figures 4.18 to 4.21, Tables 4.17 and 4.18 above it can be seen that:

1) From the changes of air size distribution, the air void system in fresh mortar with Anläggningscement is better than that with Akmenes cement. This is probably due to the fact that Anläggningscement contains lower alkali than Akmenes cement, as alkali environment in fresh concrete may destroy the air bubbles.
2) Although Sika-S can entrain more air than GYQ (for example by using Anläggningscement the air content in Sika-S and GYQ are 28.9% and 24.1%, respectively), the air contents in the small size range are almost the same when compared with the air content in real volume as shown in the figures above; for example, with Anläggningscement the total air volume below 300 μm are 3.0 ml and 3.2 ml for GYQ and Sika-S respectively measured after one hour.
3) By replacing cement with slag, the air content generally decreased. Furthermore, the effect of slag on the change of air volume was larger for GYQ than for Sika-S.
4) Normally, the air content decreased after one hour regardless of what kinds of AEAs. For GYQ used in Anläggningscement the total air content decreased while the air content of smaller air bubbles increased.
5) Sika-S acted well with Akmenes cement (kept air bubbles more stable) while GYQ acted well with Anläggningscement and Akmenes cement with slag. We may conclude that, GYQ is more suitable for low alkali cements while Sika-S is suitable for moderate ones.

5 Discussion

5.1 Discussion on the tests and the results

5.1.1 Discussion on the limitation of the tests

The measurements were supposed to imitate the practical situation of mixing and transporting the concrete with total air content measured by the gravimetric method. A drawback is that there is no standardized procedure for evaluating the air stability. Hence, a modified mortar test procedure (based on EN 196-1) was used. Although it would be closer to the actual situation if we keep mixing during the whole process, the speed of the mixer was too high as compared with the actual rotating bucket on a concrete truck. Also mixing the mortar test for ten seconds may bring some extra air bubbles in, which may bring the following measurement to deviate more from the reality. So the method used in this study should also be taken into account when interpreting the results.

Furthermore, for the AVA tests only one apparatus was available and one test took about a half hour, so it was impossible to conduct two measurements at the same time. In order to offset it, every AEA with the certain dosage was mixed and tested twice for verification. However, it is not as good as measuring the same batch of mortar twice by using two sets of AVA at the same time under the same condition.

5.1.2 Discussion on the results

In the comparison of four AEAs, it seems that BASF always showed a different behaviour compared with the other three AEAs. GYQ showed a good ability to stabilizing air bubbles at a normal dosage, but at the dosage 0.15%C it showed large increasing of air content along with the time which was strange comparing with the results at dosages 0.3%C and 0.45%C. As we know that powder is harder to weigh accurately and dilute uniformly than solution, especially at the small dosage. When the tests come to the small dosage 0.15%C everything in the test was more sensitive, which may influence the results of GYQ.

The measurement results differ between GM and AVA, the total air content measured by AVA is generally higher while better agreement is found when comparing the air content up to 0.35 mm air bubbles. The reason for this may be due to the different characteristics of measurements by GM and AVA and that the AVA is sensitive when the air contains large bubbles and when measuring large air contents. Sampling in the upper portion of the mortar for the AVA test could be another reason, because the upper portion may contain more large air bubbles. However, no clear explanation can be provided.

At the maximum air content, the spacing factors kept very stable, which are more stable than at normal dosages. That may be due to the large amount of air bubbles in the mortar, which may decrease the sensibility of spacing factor under the condition of the maximum air content.

The changes of air void system in fresh mortar are more significant for Sika-S than for GYQ with different cementitious materials when measured immediately. However after one hour it also became significant for GYQ.

The aim of this study is to find a sustainable way to improving the stability of entrained air bubbles in concrete and then reducing the usage of fine particles by entraining more amount of stable air bubbles. From Figure 4.4 and Figure 4.17, it seems that Sika-S can meet all the requirements like producing the most air bubbles with good stability especially at high dosages.

6 Conclusion and Further Studies

6.1 Conclusions

At the first stage, four kinds of AEAs were compared on their abilities of entraining and stabilizing the air bubbles in concrete.

At the normal dosages, both BASF and GYQ revealed a good capability of stabilizing the air bubbles in concrete while Sika 88 L and Sika-S seem more sensitive to the mixing before tests. For BASF, it also showed a little increase of air content within the first hour. According to the measurements by AVA, BASF can produce the most efficient air (with the bubble size <0.3 mm) among the four AEAs immediately after mixing but decreased a lot after one hour. For the other AEAs, the contents of efficient air increased after one hour. It can be concluded from these comparisons that all AEAs show their good abilities on entraining and stabilizing the air bubbles while Sika-S and Sika 88 L are little more sensitive at normal dosage.

When comparing the maximum air content, Sika-S shows the best ability of both entraining and stabilizing a high volume of air bubbles. Although Sika 88 L can entrain a large amount of air bubbles as Sika-S, it cannot stabilize them well along with the time. GYQ and BASF showed their ability of stabilizing the air bubbles but the maximum air content they can entrain in the concrete is less than Sika-S and Sika 88 L. It is obvious that Sika-S is the best choice for entraining high volume of air with a satisfactory stability.

At the second stage, three kinds of cementitious materials with two AEAs have been compared also on their abilities of entraining and stabilizing the air bubbles in concrete.

GYQ can entrain and stabilize similar amount of efficient air in both Anläggningscement and Akmenes cement, but less amount of efficient air when 1/3 of Akmenes cement was replaced with slag. Sika-S entrained less efficient air in Akmenes cement than in Anläggningscement, but when blended slag in Akmenes cement the entrained efficient air increased immediately after mixing but significantly decreased with time.

6.2 Future studies

The works in this study are only the first part of the whole study which aims at replacing the fine aggregates with the improved air bubbles. To achieve this goal the methodology for evaluating the air bubble stability should be further developed so that it is possible to more realistically simulate the real situation. In addition to testing the air in the fresh concrete, measurements should also be made on the hardened concretes. This should include both fresh and hardened properties of concrete, such as air content, air pore structure, strength and durability. Moreover, it is valuable to investigate how the fine particles can be reduced in concrete. It should also be interesting to examine how the other fine particles like quartz powder, fly ash, and lime stone filler influence the air entraining and which effect of admixtures, such as superplasticizer and viscosity modifiers, may have when entraining a high volume of air in concrete.

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Appendix A

Table A.1 Properties of Anläggning and Akmenés cements

	Name	Anläggning	Akmenés
	Type	CEM I42,5N	CEMI42,5R
		(MH/SR/LA)	
Chemical properties [wt %]	Lime (CaO) [%]	64.6	61,7
	Silicon (SiO_2) [%]	22.5	20,13
	Aluminum (Al_2O_3) [%]	3.4	4,57
	Iron (Fe_2O_3) [%]	4.2	3,22
	Magnesium (MgO) [%]	0.89	3,5
	Sulphate (SO_3) SS-EN 196-2 [%]	2.3	3.02
	Potassium (K_2O) [%]	0.62	1,07
	Sodium (Na_2O) [%]	0.06	0,18
=0,66*K_2O+Na_2O [%]	Alkali eq. ($Na_2Oeq.$) [%]	0.47	0.89
	Water-soluble chloride (Cl-) SS-EN 196-2 [%]	<0,01	0.002
	Water-soluble chromic Cr(6+) SS-EN 196-10 [mg/kg] [ppm]	<2	<2
Mineral composition [wt %]	(C_3S) [%]	54.3	54.2
	(C_2S) [%]	23.4	16,9
	(C_3A) [%]	2.0	6,7
	(C_4AF) [%]	12.6	9,8
Physical data	Specific surface(blaine) SS-EN 196-3 [m^2/kg]	317	414
	Density (compact) ASTM C188 [kg/m3]	3200	3140
	Initial setting, SS-EN 196-3 [min]	151	158
	Volume resistance [mm]	0.7	1.0

	Standard consistency, 196-3 [%]	25.2	28.0
Compressive strength [MPa] SS-EN 196-1	1 day	11.3	23.1
	2 day	21.4	37.1
	7 day		
	28 day	57.5	60.3
	Loss on ignition, SS-EN 196-2 [%]	1.1	1.1
Particle size distribution [wt %]	125 µm		99.9
	63 µm		98.9
	32 µm		82.4
	16 µm		48.6
	8 µm		26.6
	4 µm		14.7
	2 µm		8.1
	1 µm		4.1
	0,5 µm		1.4
Particle size distribution [wt %]	125 µm	99.9	
	63 µm	93.2	
	32 µm	71.0	
	15 µm	41.7	
	8 µm	24.0	
	5 µm	14.5	
	3 µm	7.2	
	2 µm	3.5	
	1 µm	0.5	

Appendix B

Table B.1 Stability of Air in fresh concrete (0.15%C)

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	0.15%C	9.34	9.72	10.02	10.27	9.89
Sika-S	0.15%C	9.77	9.3	9.6	9	9.33
Sika 88 L	0.15%C	10.69	10.5	10.32	10.13	10.51
BASF	0.15%C	10.18	9.83	10.54	10.63	10.48

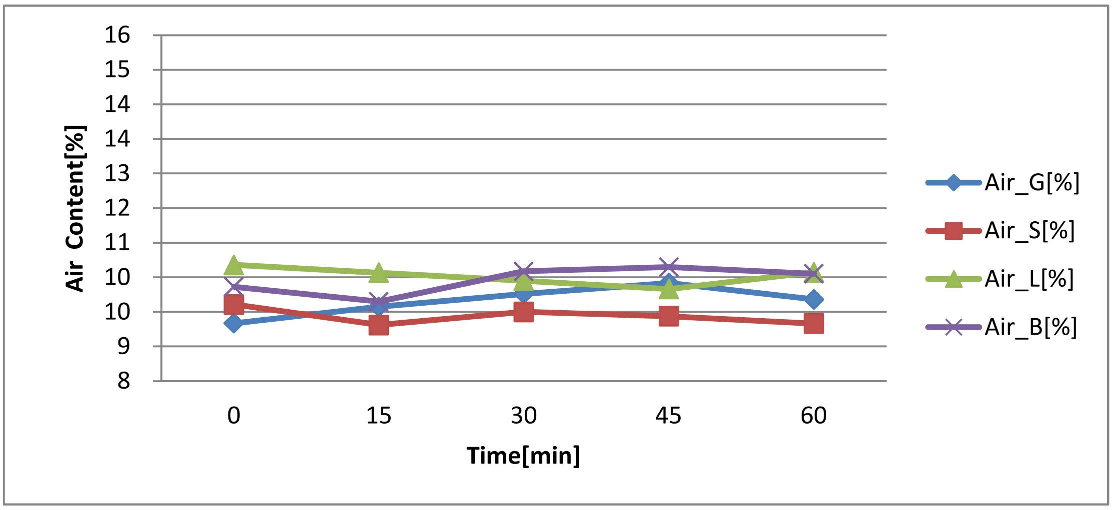

Figure B.1 Stability of air in fresh concrete (0.15%C)

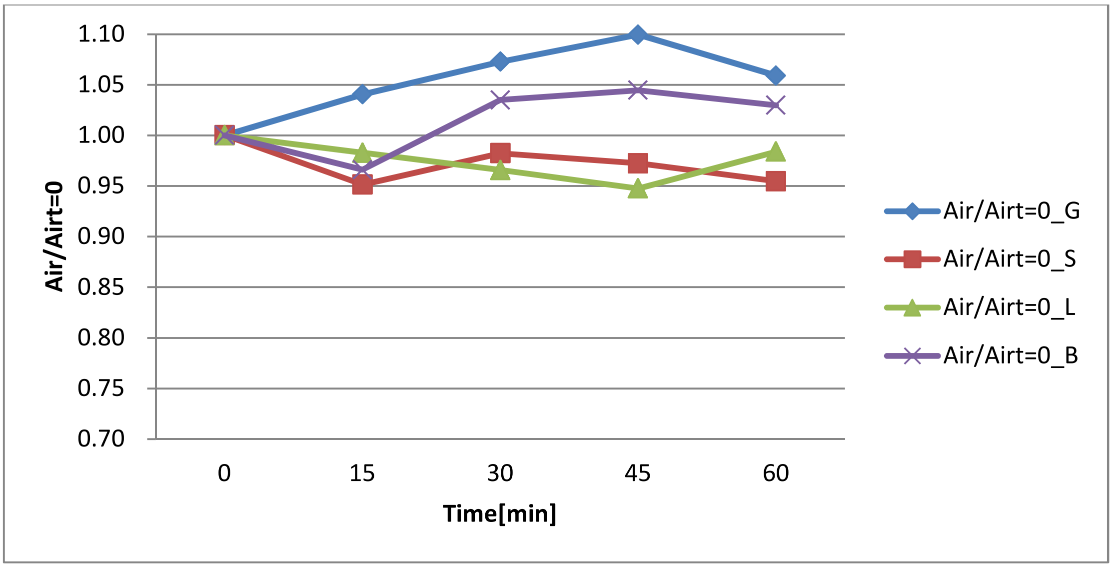

Figure B.2 Comparison of stability of air in fresh concrete (0.15%C)

Table B.2 Stability of air in fresh concrete (0.3%C)

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	0.3%C	11.32	11.07	10.8	10.9	11.32
Sika-S	0.3%C	11.33	10.85	10.4	10.45	10.17
Sika 88 L	0.3%C	12.68	12.08	11.89	11.31	11.38
BASF	0.3%C	11.53	11.46	11.83	12.4	12.04

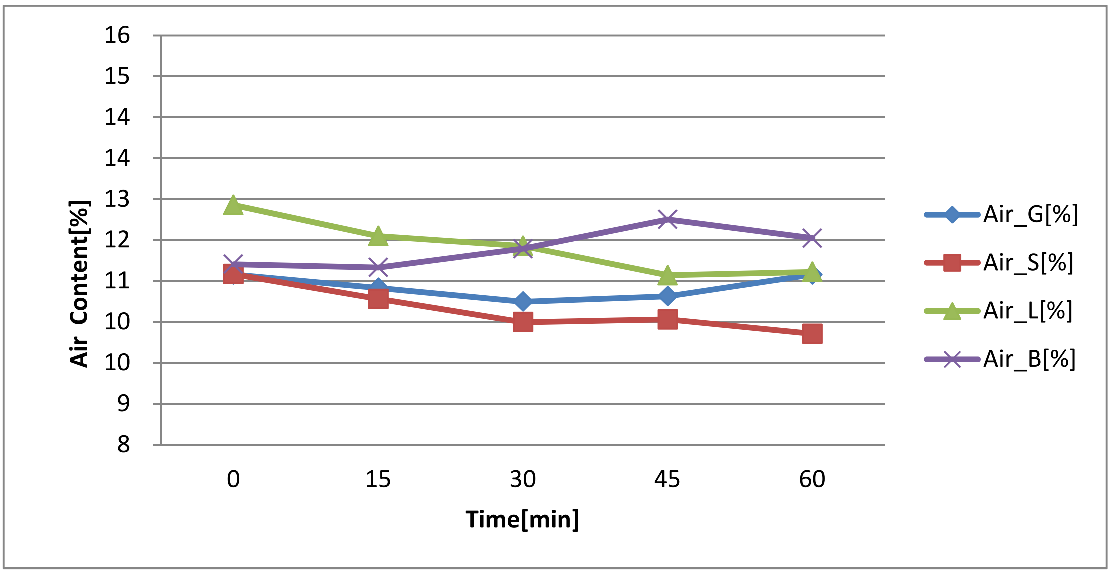

Figure B.3 Stability of air in fresh concrete (0.3%C)

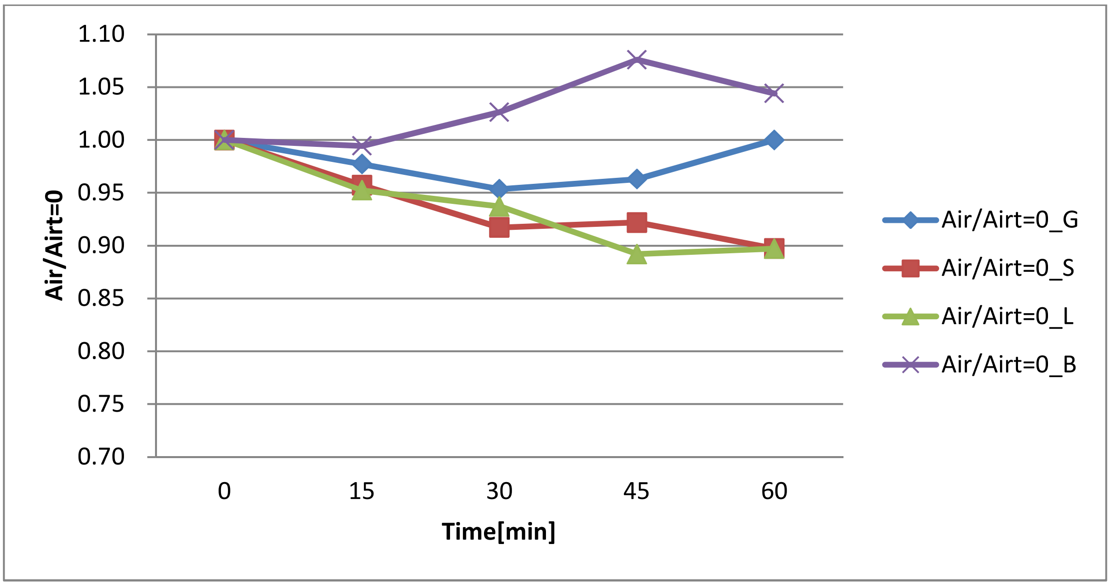

Figure B.4 Comparison of stability of air in fresh concrete (0.3%C)

Table B.3 Stability of air in fresh concrete (0.45%C)

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	0.45%C	13.36	13.02	12.52	12.53	12.59
Sika-S	0.45%C	15.57	13.98	12.87	12.44	11.99
Sika 88 L	0.45%C	15.53	14.18	14.14	13.57	13.63
BASF	0.45%C	13.44	13.03	12.58	13.15	12.81

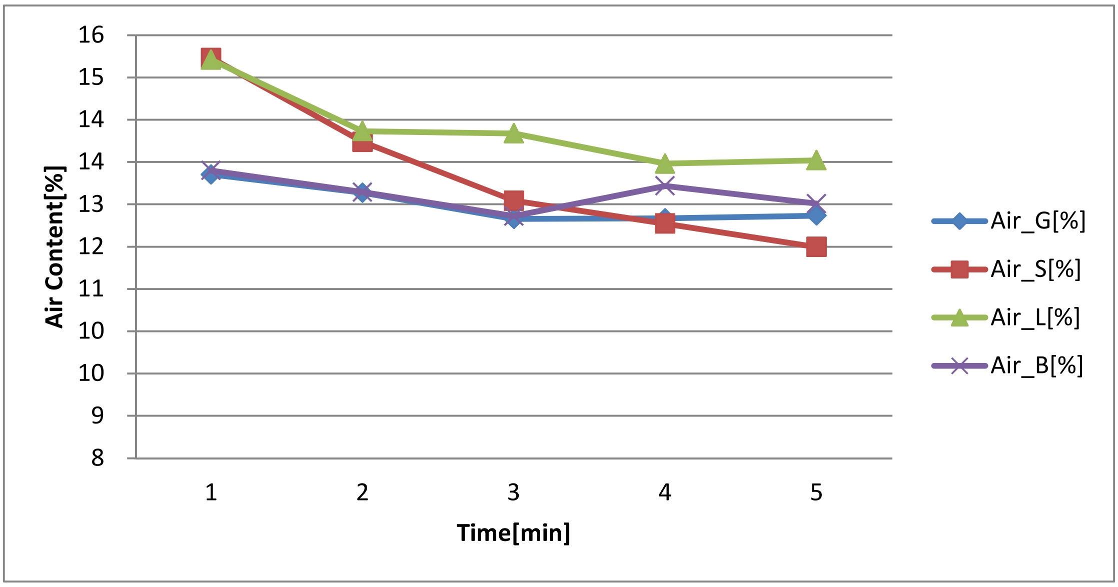

Figure B.5 Stability of air in fresh concrete (0.45%C)

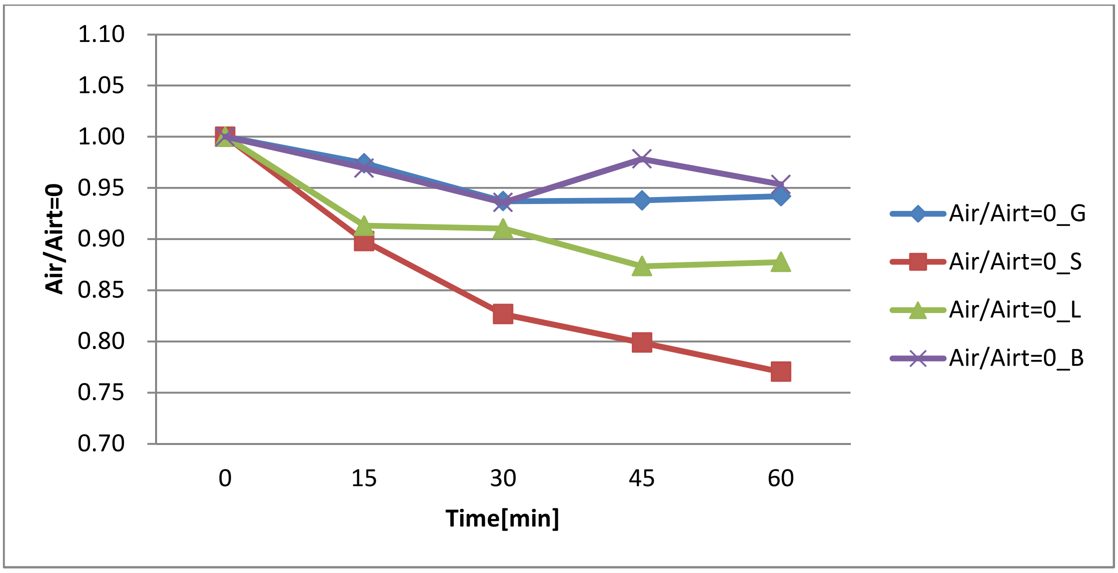

Figure B.6 Comparison of stability of air in fresh concrete (0.45%C)

Table B.4 Stability of air in fresh concrete at maximum air content

AEA	Dosage	Air content[%]				
		0 min	15min	30min	45min	60min
GYQ	3.9%C	25.33	22.92	22.4	21.9	22.13
Sika-S	4.5%C	32.12	32.31	31.72	31.53	31.13
Sika 88 L	3.9%C	30.59	27.09	25.37	24.78	24.72
BASF	3.0%C	21.4	19.7	19.74	19.88	19.93

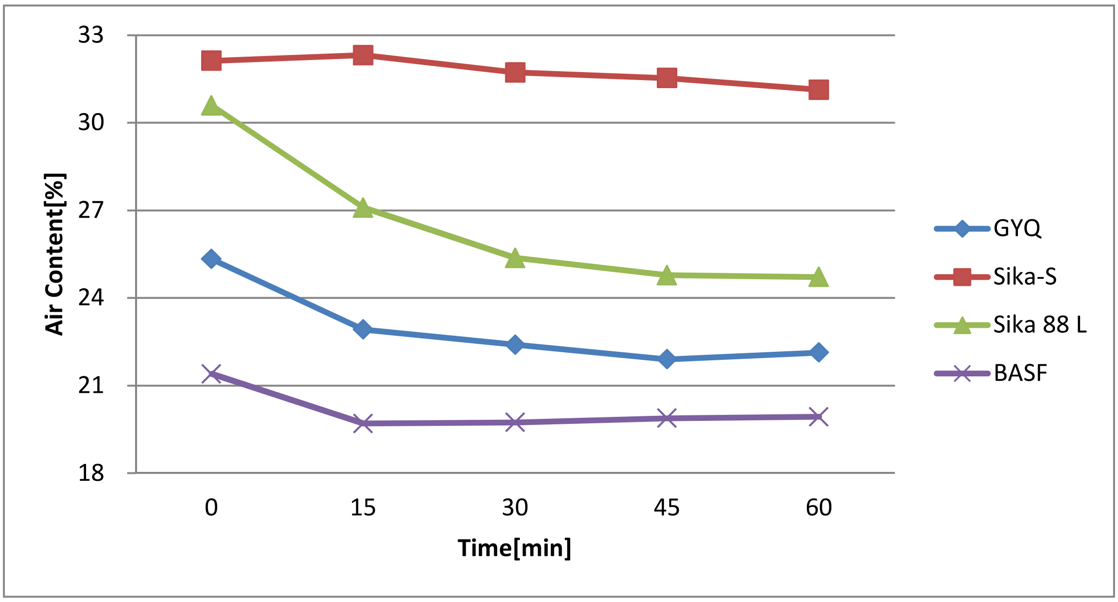

Figure B.7 Stability of air in fresh concrete at maximum air content

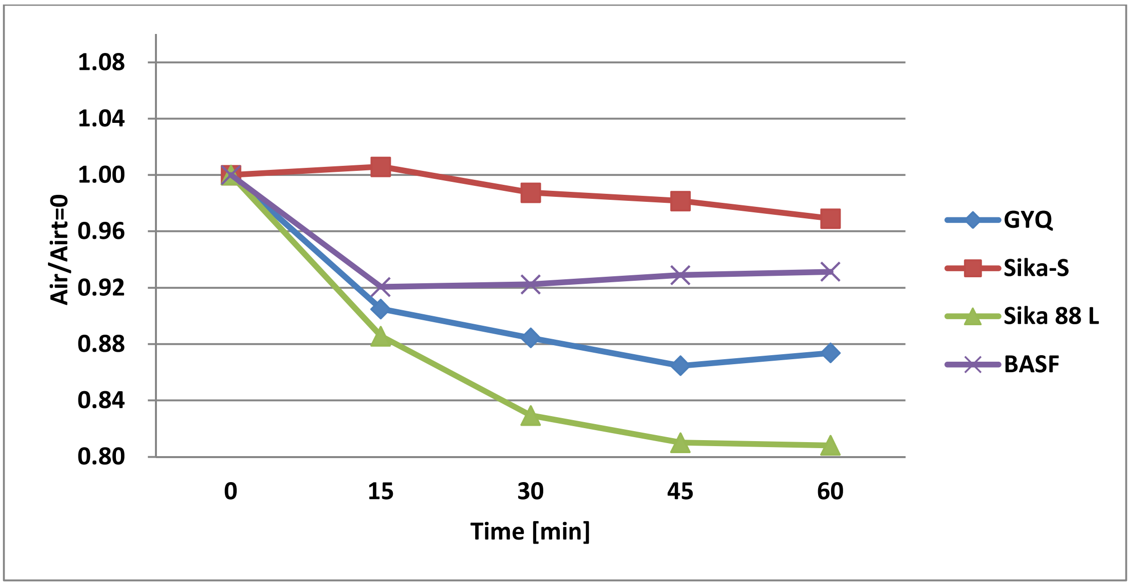

Figure B.8 Comparison of stability of air in fresh concrete at maximum air content

Table B.5 Air content measured by gravimetric method on the same sample (Limitation)

AEA	Dosage	Air content (Immediately) [%]	Air content (One hour) [%]
GYQ	3%C	24.14	20.29
Sika-S	3%C	28.88	28.41
Sika88L	3%C	28.55	20.99
BASF	3%C	20.96	18.22

Here 0.12% GYQ, 0.45%Sika-S, 2% Skia 88 L and 1.1% BASF solutions were used..

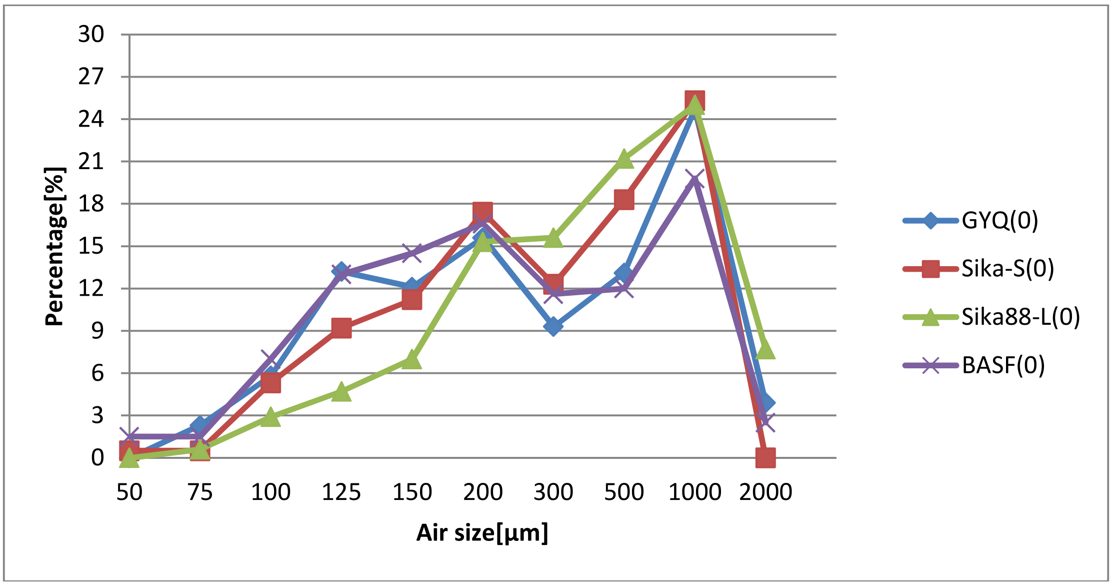

Figure B.9 Size distribution of Air in fresh concrete (3%C, immediately)

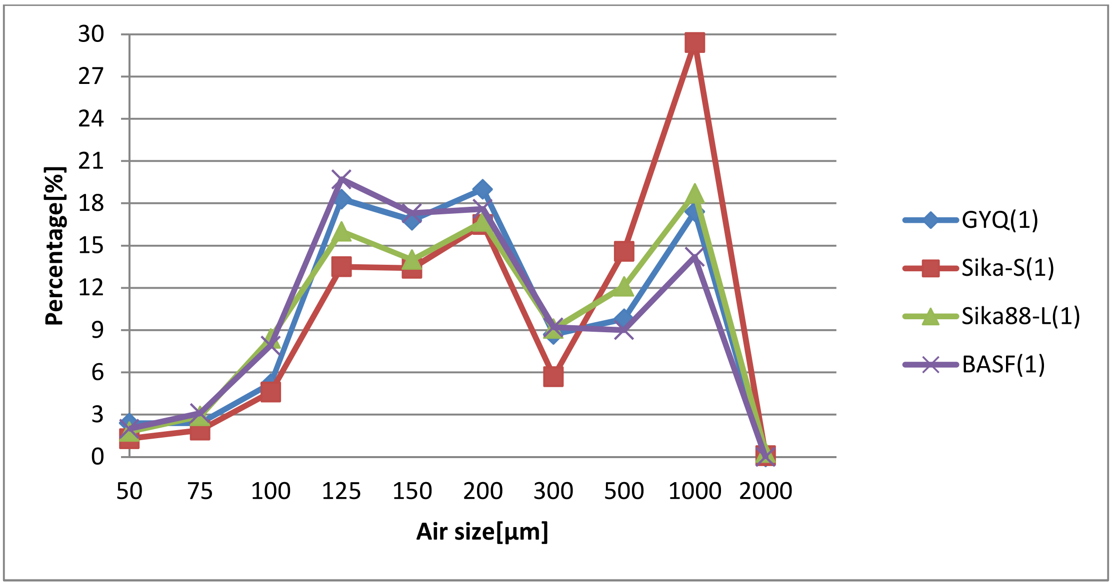

Figure B.10 Size distribution of air in fresh concrete (3%C, one hour later)

Table B.6 Comparison of air content measured by gravimetric method and AVA (Immediately)

Cement	AEA	Dosage	Air content[%]	Air content(<2mm)[%]	Air content(<0.35mm)[%]
Anläggningscement (1st)	GYQ(0.6%)	0.3%C	11.63	15.8	10.6
	Sika-S(0.45%)	0.3%C	11.94	17.3	11.3
	Sika88-L(2%)	0.2%C	12.19	7.9	1.8
	BASF(1.1%)	0.3%C	11.24	15.6	10.8
Anläggningscement (2nd)	GYQ(0.6%)	0.3%C	11.7	17.1	11.6
	Sika-S(0.45%)	0.3%C	13.2	16.1	9.6
	Sika88-L(2%)	0.2%C	11.35	16.3	11.3
	BASF(1.1%)	0.3%C	11.77	16.4	14.3
Anläggningscement	GYQ(1.2%)	3%C	24.14	28.6	21
	Sika-S(0.45%)	3%C	28.88	36.7	29.2
	Sika88-L(2%)	3%C	28.55	32.2	22.9
	BASF(1.1%)	3%C	20.96	22	16.8
CEM Ⅰ 42,5R	GYQ(1.2%)	3%C	24.75	32.8	28.5
	Sika-S(0.45%)	3%C	29.4	34.4	27.5
CEM Ⅰ 42, 5R+Slag	GYQ(1.2%)	3%(C+S)	21.46	23.5	20.1
	Sika-S(0.45%)	3%(C+S)	28.86	37.7	31.2

Table B.7 Comparison of air content measured by gravimetric method and AVA (One hour later)

Cement	AEA	Dosage	Air content[%]	Air content(<2mm)[%]	Air content(<0.35mm)[%]
Anläggningscement (1st)	GYQ(0.6%)	0.3%C	11.49	15.3	9.7
	Sika-S(0.45%)	0.3%C	11.48	15.7	10.2
	Sika88-L(2%)	0.2%C	11.86	11.2	8.8
	BASF(1.1%)	0.3%C	12.12	11.9	9.4
Anläggningscement (2nd)	GYQ(0.6%)	0.3%C	11.58	20.1	15.2
	Sika-S(0.45%)	0.3%C	12.46	21.9	14.6
	Sika88-L(2%)	0.2%C	11.6	19.8	14.3
	BASF(1.1%)	0.3%C	12.25	13.7	11.6
Anläggningscement	GYQ(1.2%)	3%C	20.29	25.7	21.7
	Sika-S(0.45%)	3%C	28.41	32.1	24.2
	Sika88-L(2%)	3%C	20.99	23.8	18.8
	BASF(1.1%)	3%C	18.22	21.6	18
CEM Ⅰ 42,5R	GYQ(1.2%)	3%C	21.03	22.7	19.8
	Sika-S(0.45%)	3%C	28.19	32.3	25.7
CEM Ⅰ 42, 5R+Slag	GYQ(1.2%)	3%(C+S)	18.55	24	14.4
	Sika-S(0.45%)	3%(C+S)	27.63	47.5	31.2

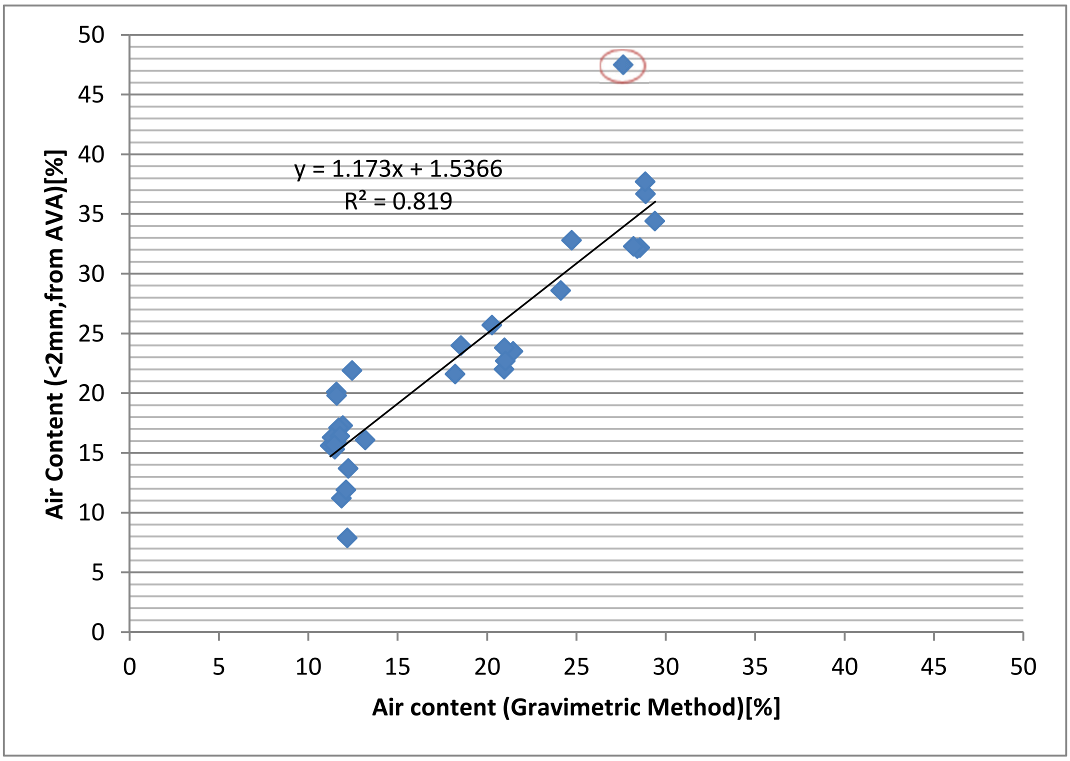

Figure B.11 *Relationship of air content measured between AVA (<2 mm) and gravimetric method*

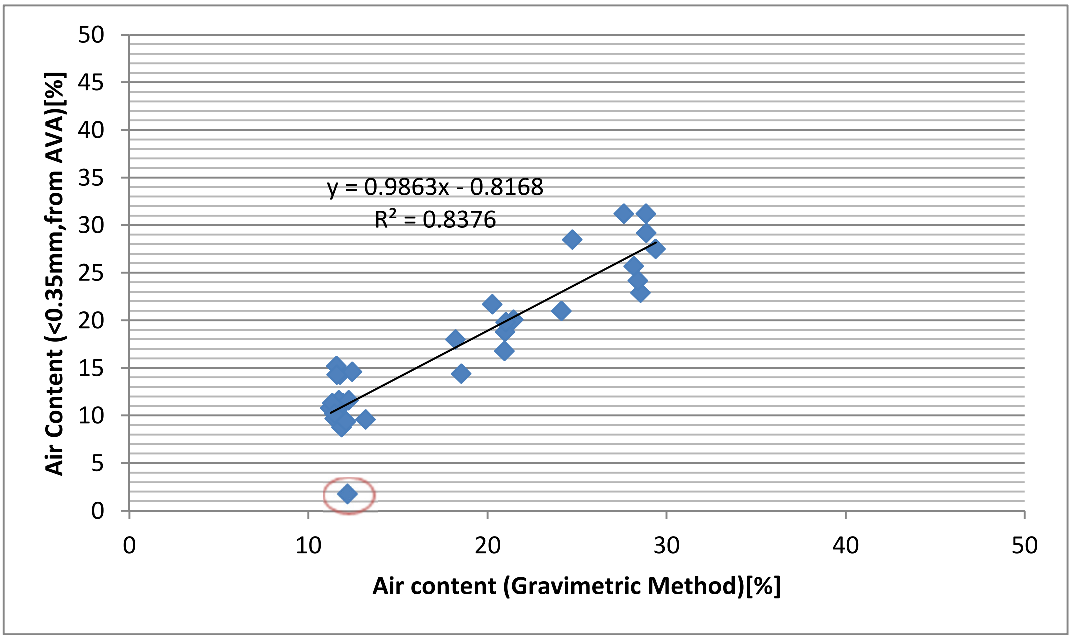

Figure B.12 *Relationship of air content measured between AVA (<0.35 mm) and gravimetric method*