Predicting AEA dosage by Foam Index and adsorption on Fly Ash

Stefan Jacobsen
Professor, Dept. of Structural Engineering
NTNU, N-7491, Trondheim NORWAY
stefan.jacobsen@ntnu.no

Margrethe Ollendorff
M.Sc Student, Dept. of Structural Engineering
NTNU, N-7491, Trondheim NORWAY
margretheo@gmail.com

Mette Geiker
Professor, Dept. of Structural Engineering
NTNU, N-7491, Trondheim NORWAY
mette.geiker@ntnu.no

Lori Tunstall
PhD Student, Dept of Civil and Environmental Engineering
Princeton University, New Jersey, USA
letunst@princeton.edu

George W.Scherer
Professor, Dept of Civil and Environmental Engineering
Princeton University, New Jersey, USA
scherer@princeton.edu

Abstract
The unpredictable air entrainment in fly ash concrete caused by carbon in fly ash was studied by measuring adsorption of Air Entraining Agents (AEA) on the fly ash and by Foam Index (FI) testing. The FI test measures the mass ratio of AEA/binder required to obtain stable foam when shaking a mixture of water, binder powder and AEA, while increasing AEA-dosage stepwise. A review of concrete air entrainment and new studies combining adsorption (TGA, NMR) of AEA on fly ash with various FI test procedures, including time dependent effects on foam stability, are presented. Inter-laboratory correlation between FI and concrete air void content verifies that FI is reliable for assessing compatible binder-admixture combinations. Our adsorption- and FI measurements showed that AEA with detectable adsorption required more AEA to foam than AEA that did not adsorb on the fly ash. Foam stability was more time dependent for adsorbing AEA. NMR showed signs of chemical changes of the AEA-FA mix after adsorption.
Key words: AEA, fly ash, carbon, air entrainment, adsorption, foam index

1. INTRODUCTION

Air voids can protect concrete against frost and salt scaling damage by being places of escape for frost-induced flow and unrestrained ice formation and by reducing the degree of saturation (Powers, Helmuth 1949, 1953, Fagerlund 1971). The increased thermal contraction as air-entrained concrete freezes, compared to freezing less or non-air entrained concrete, reduces thermal incompatibility between concrete and ice and thus avoids the glue-spall induced salt scaling (Scherer et al. 2005 a,b,c, 2007). The increased contraction results from suction in the mespores created by ice in the air voids (cryosuction). The air-entrained concrete contracts so

much when it freezes that there is less mismatch with the thermal expansion coefficient of ice, so salt scaling (which results from cracking of the ice) is reduced (Sun & Scherer 2010). The propagation of ice from air void to paste may also be affected by air void shell quality (Scherer 2011). This depends on w/b, the binder and the admixtures used. However, air voids cannot help to avoid frost and salt scaling damage in insufficiently cured concrete, over-saturated concrete, concrete with damaged pore structure due to heat curing, deleterious ageing effects etc.

In fly ash concrete, air entrainment has been reported to work as protection against frost and salt scaling in a number of studies (Bilodeau &Malhotra 1993, Malhotra and Ramezanianpour 1994, Jacobsen & Lahus 2001). In many experimental results FA concretes were found to be as frost durable as OPC concrete when certain limitations were imposed on w/b, FA/b, curing and air voids. Salt scaling durability was found to be a bit more variable than frost durability. A negative effect of slow curing on frost and salt scaling, as well as difficulties with obtaining good air-void systems in fly ash concrete, were recognized.

Problems with air entrainment in fly ash concrete have mainly been attributed to variable Loss on Ignition (LOI) in the fly ash, presumably due to (unburned) carbon (Gebler& Klieger 1983) interacting with the AEA. The Foam Index (FI) test has been used as a fast way of testing the effect of different binder-admixture combinations on air entrainment and can be useful if the fly ash is suspected of causing variable air entrainment.

This paper reviews air entrainment with focus on fly ash and experiences with FI on various fly ashes and its relation to concrete air entrainment. New studies on adsorption and characterization of AEA adsorbed on fly ash combined with Foam Index measurements are presented to help obtaining reliable and predictable air entrainment in fly ash concrete.

2.   AIR ENTRAINMENT AND FOAM INDEX

2.1 AEA and some factors affecting air content in concrete

Air entraining agents (AEA) can be described as mixtures of various surfactants. Manufacturers often provide more or less unenlightening descriptions, such as vinsol resin, tall oil, and synthetic tensides. In (Dodson 1990, Rixom 1986, Du & Folliard 2005) AEA are described as having hydrophilic (anionic, cationic and non-ionic) «heads» oriented toward the liquid and hydrophobic hydrocarbon chain «tails» oriented toward the air in the void. Their function is described as reducing water-air surface tension, adsorbing to solid surfaces and stabilizing air bubbles in fresh concrete. The distribution of AEA in fresh concrete proposed by Du and Folliard (2005) is:

$$AEA_{added} = AEA_{interface} + AEA_{adsorbed\ on\ solid} + AEA_{liquid} \qquad (1)$$

This is over-simplified, as it neglects the kinetics of adsorption, which leads to exchange of molecules between the terms on the right side of the equation.

After the formation of air bubbles, they may disappear, change or collapse in fresh concrete due to migration to the surface, diffusion of air from small to large bubbles, dissolution of air from bubbles into liquid, and coalescence of two or more bubbles due to capillary flow (drainage) between bubbles (Fagerlund 1990, Du & Folliard 2005). Fagerlund (1990) calculated that air bubbles with diameters below 20 – 40 microns in fresh paste of w/c = 0.50 can dissolve in the water around the void. Dissolution occurs because the higher air pressure ($p = 2\gamma/r$) generated

by the surface tension, γ, in voids with smaller radius, r, enhances the solubility of air in water. The water becomes saturated with air as the small voids dissolve, so the air diffuses to the larger voids causing them to expand, resulting in increased total air volume. Both the dissolution of air and the diffusion of air from small to large bubbles depend on several factors, including the volume fraction of water in the fresh paste and tightness of the air void wall (Fagerlund 1990, Gutman 1988). Fagerlund estimates that a 10 µm bubble could dissolve in 10-30 minutes. He also notes that the AEA and other organic additives encourage formation of smaller air bubbles, so the changes in the distribution during the induction period could be substantial.

Change and disappearance of air voids might also be due to other mechanisms related to foaming and forces acting in solid-liquid-gas emulsions: lifting (buoyancy, momentum) and downward resistance (drag, surface tension, particle-bubble collisions) (Yang et al. 2007). This implies that rheology of fresh concrete also plays a role in the movement and viscous drag on air voids due to the rate of shear of the fresh concrete. Thus, in practice air entrainment consists of several effects acting concurrently with the stabilizing effect of AEA.

Air content increases in more or less the same way with increasing AEA dosage for pure paste (binder, water, admixture), concrete and mortar (Joliceur et al. 2003). However, the entrained air volume is much higher in mortar than in concrete, whereas pure paste gets lower air entrainment than mortar and concrete for a given AEA dosage (Joliceur et al. 2003, Hammer and Johansen 2005). This even holds when comparing air void content by paste volume fraction, so apparently aggregate affects air entrainment. Capture of fine air voids in the paste between fine sand particles in the fraction 0.3 – 0.6 mm is suggested (Rixom 1986). According to Geiker & Kjær (1995) the air voids captured between the fine sand particles (0.15 – 0.6 mm) are the ones stabilized by AEA, thus affecting air pore structure. Crushed aggregate might disperse air better than natural gravel (Rixom 1986, Du & Folliard 2005). However, increased content of fines smaller than ~20 microns reduces air, as the fines in pozzolans do (Rixom 1986).

A few other rules of thumb for varying air volume in fresh concrete are found in the literature. Increased temperature reduces air content. This is probably mainly owing to less available AEA due to adsorption on hydration products and also complex chemical-physical mechanisms related to reaction, coagulation and precipitation of AEA that reduce the air entraining effect with increased temperature (Du & Folliard 2005, Rixom 1986 p.107,117, Dodson 1990 p.135,137). Thus the physical effects of reduced solubility of air in water and increased pressure in air at increased temperature do not seem to relate to change of concrete air content at increasing temperature. Prolonged mixing (> 5 – 10 min) reduces air content (Rixom 1986).

The effect of rest, transport, pumping/distribution, placement compaction and pressure can be assumed to reduce fresh air content, depending on the stability of the air void system (Geiker & Rostam 1995, Du & Folliard 2005). Contradictory reports on the effect of pumping on air void content exist. Traditional plastic consistency concrete with 320 kg/m^3 was reported to have increased air-void content after pumping (Johansson & Tuutti 1976). Concrete with superplasticizer is more easily air entrained than concrete with less flow, but is also more susceptible to loss of this air during pumping (Kaplan 2001, Spiratos et al. (2003) p.110). Highly flowable concrete with superplasticizer, including HPC concrete, showed reduced air content in hardened concrete after pumping in several studies. Air voids less than ~50 microns were found most susceptible to disappear, more so after vertical than after horizontal pumping (Pleau, Pigeon, Lamontagne, Lessard 1995). Geiker and Rostam (1995) studied air content and air void structure in 17 different mixes as function of pumping and pumping conditions. They found reduced total air content, reduced content of voids < 0.35 mm, and increased spacing

factor after pumping in practically all tests. Prolonged time under pressure was found to have an extra effect on reducing air content. Furthermore, their tests included comparable concrete mixes with OPC and OPC+fly ash, but no clear difference in loss of air voids could be discerned. Pleau et al. (1998) found that the air void structure may not necessarily be completely destroyed by job-site pumping, since the number of very small voids that contribute most effectively per unit volume to spacing and surface was still very high after pumping. The spacing factor in hardened w/c = 0.43 concrete (100 mm slump) increased from 0.18-0.20 mm before to 0.22-0.31 mm after pumping. For w/c = 0.30 concrete (200 mm slump) a much larger increase in spacing factor in hardened concrete was found in the same study: from 0.18-0.22 mm before to 0.43-0.49 mm after pumping. Lepage et al. (1998) investigated pumpability and effect of pumping on air void structure in w/b = 0.38 (70-90 mm slump) and w/b = 0.30 (110-210 mm slump) concretes with hydroxycarboxylic acid water reducer and fatty acid based AEA. Air void spacing in hardened concrete was less affected by pumping for the w/b = 0.38 concrete (0.12 – 0.13 mm before and 0.14-0.16 mm after pumping) whereas the w/b = 0.30 concrete had more serious damage to its air void system by the pumping (0.18-0.23 mm before and 0.42-0.49 mm after pumping). Jensen, Hasholt and Geiker (2005) studied the air void stability in SCC as affected by formwork pressure during curing. They found that Boyle-Mariottes law applies for prediction of air content in pressurized fresh concrete. A fair prediction of increased spacing and reduced specific surface in hardened concrete could be made assuming equal pressure on all voids with the standard equation for Powers spacing factor. Full scale pumping tests showed that pumping from bottom was more destructive to the air void structure than pumping from top.

Thus the void spacing is most increased by pumping in highly flowable concrete by increased pressure, particularly at form filling from below. Prolonged pressurization time further reduces the air content and increases the spacing. An effect of fly ash on loss of air during pumping has not been observed.

2.2 AEA dosage and stability with fly ash, silica and different OPC cements

Generally, an increased AEA dosage is needed when adding pozzolans, such as fly ash (Malhotra and Rameizanpour 1994) and silica fume (Sellevold and Nilsen 1986), to maintain a constant air void content. Presumably the increased specific surface of the binder plays a role. In fresh silica fume concrete, a higher stability of the entrained air was found compared to OPC-concrete (Sellevold and Nilsen 1986) and compared to FA-concrete (Geiker & Kjær 1995). Increased cement fineness also reduces air content, or increases necessary AEA dosage to obtain a given air content, whereas increased cement alkali content increases entrained air (Dodson 1990, Du & Folliard 2005).

The effect of fly ash on the stability of air void content in fresh concrete seems to be less known, except for all the problems reported related to variable carbon content of the fly ash mentioned in Section 1. In general, the effect of increased LOI or carbon content is to reduce air content (or to increase the necessary AEA dosage). The reason for this is presumably that the carbon adsorbs AEA, owing to its high surface area and/or strong chemical affinity, thereby reducing available AEA and thus air entrainment (Gebler and Klieger 1983). The approach proposed to solve this issue has been to increase the AEA dosage or switch to a product that works, mainly on an empirical basis. The difficulties in predicting the effect of air entrainment also includes effects of the many possible combinations of admixtures, binders, concrete mixes and practical circumstances.

2.3 Foam Index and air content in concrete at varying LOI and/or carbon content

Foam Index testing

The foam index (FI) test was originally developed by Dodson (1990) to test the effect of variation of Portland cement characteristics (specific surface, alkali content) on air void formation in concrete. It has been used to assess the effect of fly ash on air-void formation (Gebler and Klieger 1983, Baltrus et al. 2001, Külaots 2003, Vestgarden 2006, Harris et al. 2008a,b,c, Ollendorff 2011). The FI test, in brief, consists of shaking a mixture of water and binder powder (typically w/b = 2 – 2.5), and increasing the AEA dosage stepwise until stable foam forms on top. We use an automated Griffin flask shaker with 2.4 Hz frequency and modified with an arm giving 20 mm amplitude to agitate a plexiglass container with 70 ml volume and 40 mm inner diameter; shaking for 60 seconds is used to mix water and binder, and then 15 seconds shaking with AEA. The stability of the foam forming on top of the slurry is then observed while at rest for 45 seconds. If the surface does not remain covered with stable foam, the AEA dosage is increased with a pipette, then shaking for 15 seconds and observation for 45 seconds is repeated until stable foam covers the surface. The FI is then simply the concentration of AEA in ml/kg binder when the foam remains stable.

Figure 1 shows the results of FI testing of 3 different low-lime fly ashes (1.0, 3.1 and 3.9 % carbon with Blaine surface area of 357-359 m^2/kg) from Europe provided by Norcem, a Norwegian Norcem CEM I 52.5 OPC with Blaine = 360 m^2/kg, and one test on pure water (Ollendorff 2011). The air entraining agent was Sika Aer-S which is described as "synthetic tenside" according to the product sheet. The test with only 25 ml of deionized water had ≤ 5% lower filling than the tests with w/b = 2.5 slurries, due to absence of binder volume (~3 ml). Each curve is the mean of 3 parallel samples except for the OPC, where 6 parallel samples were used. Scatter was lowest for low carbon FA (Coefficient of Variation = 1 %), a bit higher for water and OPC (CV = 4 %) and highest for high carbon FA (CV = 8 and 12 % for 3.1 and 3.9 % carbon respectively).
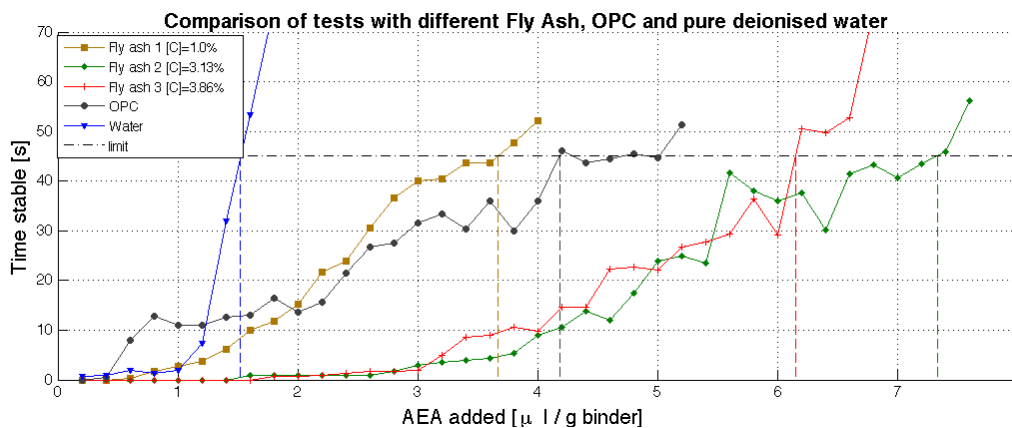

Figure 1 – Foam Index (µL/g) of 3 fly ashes, 1 OPC CEM I 52.5 and only deionized water (Ollendorff 2011)

Figure 1 shows that AEA and pure water foams easily in the shaker at very low AEA dosage. The AEA dosage with only water is calculated per 2.5 g of water. A much higher AEA dosage was required to obtain foam when introducing powder particles. The low-carbon fly ash and the pure cement each showed rather low, and similar, FI. That is, these two types of particles had approximately the same effect on foaming. The two high-carbon fly ashes had higher FI, as expected. The recommended normal dosage of this AEA in concrete is 0.01 – 0.08 % of cement weight = 0.1 – 0.8 µL/g which is only in the order of 2 – 20 % of the dosage required for stable

foaming in the FI-test. This difference can be due to different mechanisms of air entrainment in concrete (stabilization) than in the FI-test (foaming). However, as we shall see, experience shows a correlation between FI and air entrainment in concrete.

In Tables 1 and 2, compilations of various foam index test results on different fly ash binders and AEA are shown. Table 1 shows that the FI test conditions applied by the different authors vary with respect to drop size, AEA dilution, sample- and container size. In addition the shaking was often done manually, thus probably varying somewhat between the tests. Harris et al. (2008a,b,c) proposed a standardized FI test based on experience with different FI test procedures on 4 different fly ashes. In their tests, the coefficient of variation went up to 20 % when doing 3 parallel FI tests on each type of ash with 4 different FI test procedures, of which only the results of the procedure correlating best to concrete air void content is shown in Tables 1 and 2.

Figure 2 shows the evolution of foam during the standard test for the high carbon ash shown in Figure 1. Figure 3 shows the different structures of stable foams on the 3 ashes in Figure 1. It is seen that the nature and structure of the foam varies (bubble size, foam volume) both during propagation, as the foam gradually fills the surface before the test end point, and as stable foam is reached (Ollendorff 2011).

Table 1 - Test conditions in FI tests

Reference	w/b	AEA dilution	Drop size	Shake	Rest	Volume container	Binder
			μL	sec.	sec.	mL	g
G&K	2.5	1:43	?	15	45	473	20
Baltrus	2.5	1:40	50	15	15	15	2
Külaots	2.5	1:9	20	15	45	70	10
Vestgarden	2.5	1:9	20	15	45	70	10
Harris bottle	2.5	1:19	10	15	45	132	10
Ollendorff	2.5	1:9	20	15	45	70	10

Figure 2 – Evolution of foaming in 40 mm diamter FI test container of high Carbon fly ash in figure 1 (Ollendorff 2011)

Figure 3 – Varying foam structures at stable foaming of (from left) ash No. 3, 2 and 1 in figure 1 (Ollendorff 2011)

Table 2 shows a selection of data from (Gebler and Klieger 1983, Baltrus et al. 2001, Külaots 2003, Vestgarden 2006, Harris et al 2008a,b,c) together with the new results (Ollendorff 2011). Within each of these studies it was found that the AEA dosage needed to obtain stable foam increases with increasing carbon content and/or increasing loss on ignition of the fly ash. Comparison should preferably be done within the same series of tests due to the different procedures. Furthermore it is not clear from the data whether carbon or loss on ignition is best related to FI.

Table 2 - Foam index for combinations of AEA and fly ash binders with varying LOI

Ref	AEA	Binder	Carbon % of mass	LOI % of mass	FI μl/g binder
G&K	Vins.Res.	80%OPC+20%FA	0.1/1.2/4.2	0.4/1.8/4.9	4.5/6.5/12
Baltrus	Darex 2	FA	0.3/4.0/14.6	-	50/24/66
Kulaots	Darex2 Air 40	80%OPC+20%FA	-	6.1 66/21	15 133/60
Vestgarden	Micrair100 Fatty acid	1 SR OPC, 9 different 20%FA	*-3.8	1.4-4.7	11-47
Harris et al	Wood Rosin	80%OPC+20%FA	-	0.8/0.4/0.1/0.6	10/7/6/3
Ollendorff (Fig.1)	Sika Aer-s synt.tens.	OPC, FA or only water	**/1/3.1/3.9	2.5/1.1/3.6/4.5	4.2/3.7/7.3/6.2

*, **: not measured (sulphate resistant low-C_3A OPC, OPC)

Relation Foam Index – air content in concrete
The usefulness of the FI test depends, of course, on its ability to predict air content in concrete. Measurements of air content in fresh concrete made with the same ash and AEA as in the FI test, however, were only published in a few cases (Gebler & Klieger 1983, Vestgarden 2006, Harris et al. 2008). FI was correlated to air content or AEA dosage in concrete in various ways for different types of AEA and fly ashes.

Gebler and Klieger (1983) used constant concrete consistency and air content at variable AEA concentration and w/b = 0.40-0.48 (Vinsol resin and no Water Reducing Agent (WRA)) with different ashes. The concrete mixes were carefully made without water reducer to obtain 6 ± 1 % air by varying the Neutralized Vinsol Resin AEA dosage and adjusting w/b so that slump

varied between 3 and 4 inches (~75 - 100 mm). The correlation between FI and AEA dosage for 6 % air in a linear plot was $R^2 = 0.93$ for 10 ashes /1 OPC reference.

Figure 4 shows a plot of FI versus air content in fresh concrete, based on the data by Vestgarden (2006). He used constant dosage of AEA (0.18 kg/m^3 of fatty acid polyglycol type AEA and polycarboxylate high range WRA (= Super Plasticizer - SP[1]) in a constant concrete composition of w/b = 0.41 with 10 different ashes and 1 control mix. All mixes had 2.4 kg of co-polymeric water reducer and 420 kg binder (20 % FA, 5 % SF and one reference without FA). The slump immediately after mixing varied in the range 165 – 225 mm. The correlation between FI (our automated shaker) and fresh air void content after 10 minutes in a power function was $R^2 = 0.84$ for 9 ashes/1 OPC reference.
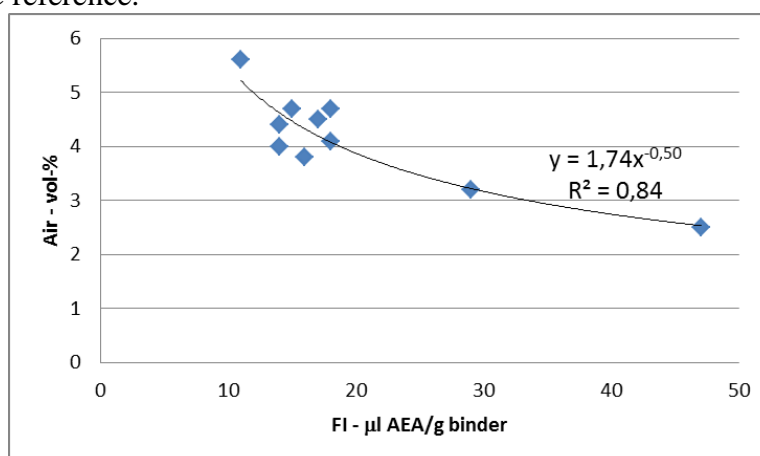

Figure 4 - FI vs air content in fresh concrete after 10 minutes (Vestgarden (2006))

In the study by Harris et al. (2008a,b,c), AEA was added to obtain constant concrete air-void content of 6.0 % at constant w/b = 0.45 (wood rosin type AEA and ASTM C494 type D WRA) with 4 different ashes. This work showed best correlation coefficient $R^2 = 0.94$ in a linear plot between FI (bottle-type FI test) and AEA dosage to obtain 6.0 % air in fresh concrete.

Note that in the 3 cases cited above, the FI tests were made with only AEA, binder and water, whereas in concrete two of the test series combined WRA and AEA and one of the concrete series in addition contained silica fume. Considering the wide variation in materials and test conditions, this indicates that the FI-test is useful for inter-laboratory prediction of the effect on concrete air entrainment of varying AEA-Fly ash combinations.

Foam tests with combinations of AEA and water reducers
The effect of combinations of AEA and WRA on air entrainment can be difficult to predict. According to Rixom (1986) lignosulphonate and hydrocarboxylic AEA work with WRA, and also alkyl-sulphate AEA can work with WRA. Pre-screening tests of admixtures include foam stability tests, in addition to FI tests. While the FI uses a water/binder ratio of ~2.5 and often a similar binder composition as the concrete, foam stability measurements are made with only liquid and admixture or a w/b ratio in the order 10 – 50. These are thus even further away from concrete than the FI-test. Foam stability measurements have been used to study the chemistry of surfactants for a long time and the foaming has been correlated to surface viscosity, see for example (Brown et al. 1953, Shah et al. 1978). In the foam stability test, the aqueous solution with admixture is usually shaken in a tall glass. The foam volume gets much larger than in the

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[1] The term SP is used in Europe while High Range WRA is used in North America.

FI test and the foam stability is measured over more than an hour. A variety of such foam stability tests have been used on AEA-solutions.

Studies of foaming and surface tension of mixtures of WRA and AEA and subsequent studies of air entrainment in concrete including air void structure (Eriksen & Andersen 1986) showed that melamine-type WRAs worked with both AEA based on "synthetic tenside" and on "vinsol resin", whereas naphthalene-type WRA worked with vinsol resin. These 3 AEA-WRA combinations were the only ones that both gave good foaming and good air void systems in hardened concrete (Eriksen & Andersen 1986). The studies showed no clear relation between foaming and measurements of surface tension in the foaming solution. Based on foam stability measurements combined with microscopy observations of bubbles and freeze/thaw testing of concrete, it was claimed that bubble wall thickness is important for concrete air void stability and freeze/thaw durability (Gutman 1988). Foam meter studies of AEA with low-alkali cement containing 6 % silica fume, 12 % fly ash, and different WRA/AEA combinations, showed medium foaming and some loss of foam during 90 minutes, compared to when these admixture combinations were used with pure OPCs or pure slag (Sørensen and Geiker 1995, HPC Specification Dansk Betoninstitut 1995).

AEA and AEA-WRA combinations were studied in fresh concrete aiming to find solutions robust against variable fly ash carbon content (Nkinamubanzi et al. 2003, Vollset & Mortensvik 2011). The latter work showed that stable air pore structure can be obtained with AEA and polycarboxylate-based SP in flowing consistency concrete that was not pumped. However, both studies provide limited applicability for concrete technologists, beyond telling what brand names to choose.

Ready-mix concrete producers typically have standard solutions that work most of the time. For high slump concrete (typically 200 mm slump) co-polymer water reducing agents are usually mixed a bit before AEA is added as the final constituent to the mix. On-site problems with unstable air content are, however, common (Mørtsell, Heidelberg Cementgroup pers. comm. 2011) and robust solutions are therefore needed. Vestgarden (2006) used the FI test to assess AEA-WRA combinations and mix procedures by combining two different polycarboxylate SP with "tenside" AEA with one powder mix (75 % OPC and 25 % FA) with low/moderate carbon content, applying 4 different FI-test procedures:

- only AEA
- AEA+SP mixed in simultaneously
- SP first, then AEA
- AEA only, then adding SP "dropwise"

FI decreased somewhat when mixing AEA and the SP simultaneously (FI = 28 μL/g) compared to FI obtained with only AEA (FI = 32 μL/g). Adding SP and mixing a bit first with water and powder, and then adding AEA further reduced FI (= 24 μL/g). The fourth FI procedure, with first adding AEA, water and binder powder and producing stable foam, and then adding the SP and continuing shaking, showed less and less foam as more SP was added. Apparently this delayed SP addition caused very high effective FI. There were only minor differences, if any, in the effects of the two types of co-polymeric super plasticizers. Thus it seems that the lowest FI corresponds to the above referred mixing sequence preferred in practice.

To sum up, both type of AEA and WRA as well as the mixing transport, placement/casting and compaction affect air entrainment. More knowledge is needed to find generic materials that work together and to understand the mechanisms of air entrainment.

3. COMBINING AEA ADSORPTION ON FA WITH FOAM INDEX

Following the studies with TGA and NMR (Tunstall & Scherer 2011) of AEA adsorption on fly ash, Foam Index measurements were made on the same materials (Ollendorff 2011). Two fly ashes with low and high carbon contents were selected from the US market. These two ashes had 2.4 % and 11.73 % LOI and 1.7 and 6.7 m^2/g BET surface areas, respectively. In addition, 4 different AEA from the US market were investigated: Saponified Rosin (SR), Synthetic Olefin Sulfonate (SOS), Saponified Tall Oil (STO) and Neutralized Vinsol Resin (NVR).

3.1 Adsorption measurements

A Perkin-Elmer TGA was used on various quite concentrated AEA solutions. First AEA solutions that had not been mixed with FA were run through the TGA temperature cycle to measure the residual solids content of each AEA. TGA measurements were made on the supernatant of solutions of AEA that had been exposed to fly ash and then filtered, thus giving the amount of AEA retained in the solution (i.e. not adsorbed on the FA). In addition ^{1}H NMR spectra were made of selected pure AEA and AEA after mixing with varying amounts of selected Fly Ash using a Bruker Avance III NMR instrument (Tunstall & Scherer 2011).

3.2 Foam Index (FI) measurements

Three different foam index test procedures were run on combinations of the US Fly Ashes and AEA. The FI testing was made with the automated shaker described in section 2.3, Figure 1 and Tables 1 and 2. In addition to the "standard" procedure, "short" and "long" tests were made to investigate the effect of adsorption on foaming and foam stability (Ollendorff 2011). For all these tests two parallel samples were run.

"Standard" FI test
The 70 ml container with 40 mm inner diameter was filled with 10 g fly ash and 25 g distilled water and an initial 60 seconds shaking was done with 2.4 Hz frequency and 20 mm amplitude. Then one 20 μL drop of 1:9 AEA solution was added, followed by 15 seconds of shaking. If the foam was not stable after 45 seconds then another 20 μL drop of 1:9 AEA solution was added and the cycle [15 seconds shaking and 45 sec waiting while observing for stable foam] was repeated. This was done with a sufficient number of AEA drops to obtain stable foam. FI was calculated as μL AEA/g binder when stable foam was observed, as shown in Figure 2.

"Short time" FI test
In this FI test, half the amount of AEA determined in the "standard" FI test was added after 60 seconds of initial mixing. Then the mix was shaken for 15 seconds and observed for 45 seconds to determine foam stability. If necessary, the procedure [a 20 μL drop of AEA solution added, 15 seconds of shaking and 45 sec waiting] was repeated until the foam remained stable.

"Long time" FI test
In this FI test, the sample from the "short time test" with stable foam was left with the lid on for 1 hour. Then, if the foam was still stable "Long FI" = "Short FI". If the foam had disappeared,

then one 20 μL drop of 1:9 AEA solution was added, followed by 15 seconds shaking, and 45 seconds observation. In this way, both foam stability and effect of adsorption kinetics on necessary additional amount of AEA to regain foam was determined.

4.   RESULTS AND DICUSSION

Figures 5 and 6 show adsorption determined by TGA for concentrated Saponified Rosin (SR) and Synthetic Olefin Sulfonate (SOS) exposed to high carbon fly ash.
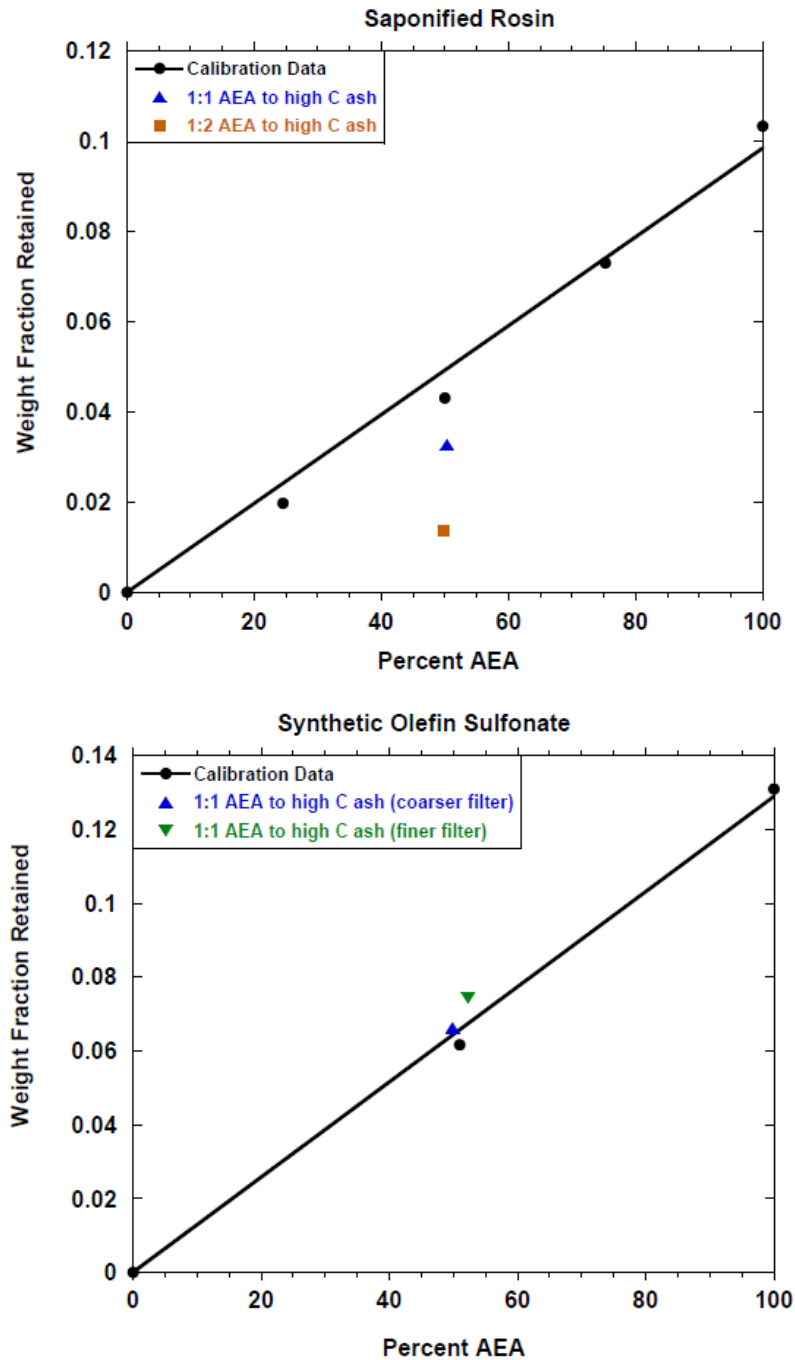

Figure 5 – Adsorption of SR AEA (upper) and no adsorption of SOS (lower) on fly ash determined by TGA(Tunstall & Scherer 2011)

Figure 5 shows that adsorption differed between the different types of AEA expressed as % AEA added versus residual AEA in the solution. There was detectable adsorption of Saponified Rosin, whereas there was no detectable adsorption of Synthetic Olefin Sulfonate (SOS), Saponified Tall Oil (STO), nor Neutralized Vinsol Resin (NVR) on high-carbon fly ash. Similar results as those of SOS shown in Figure 5 were thus obtained for STO and NVR.

Furthermore, the preliminary NMR studies (Tunstall & Scherer 2011) revealed a selective adsorption and/or chemical change in the AEA-FA mix of certain AEA ingredients or some other kind of interaction, as shown in Figure 6. As a simplified description, the positions of the peaks in Figure 6 represent the species present, whereas the peak sizes represent the amounts of the different species.
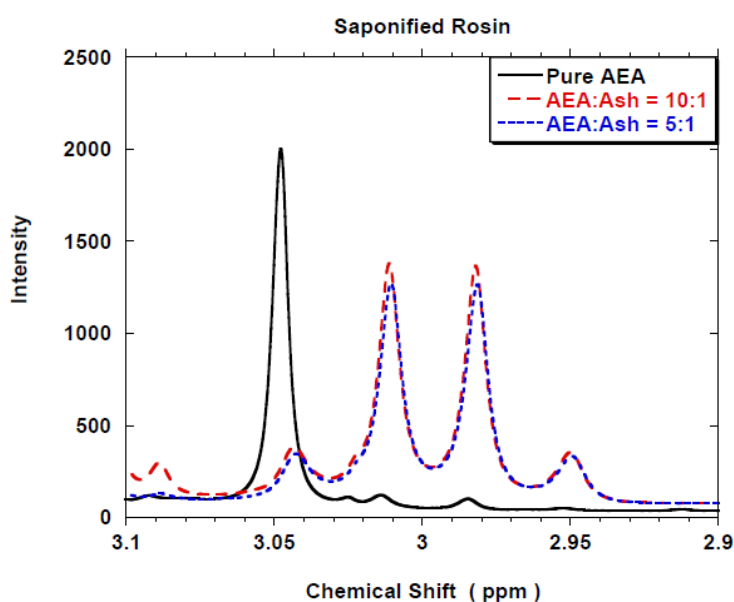
Figure 6 – ^{1}H NMR spectra for AEA without and with adsorption on high carbon FA (Tunstall&Scherer 2011)

The Foam Index tests were run after the adsorption measurements. The two air entraining agents SR (adsorption) and SOS (no adsorption) that are shown in Figure 5 were selected for all three types of FI tests described in the previous section (standard, short, long) on low- and high carbon fly ash. In addition the standard FI test was run on Neutralized Vinsol Resin (NVR) with high carbon fly ash. Table 3 shows the results of the "standard" and the "short" tests whereas table 4 shows the results of the "long" test. All results are mean values of two parallel samples.

Table 3 – Foam Index test results with "standard" and "short" procedure

AEA	Fly Ash	Procedure	FI (μL/g)
SR	High Carbon	Std	193
	High Carbon	Short	*104*
	Low Carbon	Std	18.4
	Low Carbon	Short	*17.6*
SOS	High Carbon	Std	40
	High Carbon	Short	**36**
	Low Carbon	Std	4.8
	Low Carbon	Short	**4.8**
NVR	High Carbon	Std	32

Table 4 – Foam Index test results with "long" procedure

AEA	Fly Ash	Stable time (sec)	Additional (µL/g)	FI (µL/g)
SR	High Carbon	22.9	*48*	*152*
SR	Low Carbon	35	*4.8*	*22.4*
SOS	High Carbon	≥ 45	0	**36**
SOS	Low Carbon	≥ 45	0	**4.8**

Table 3 shows that the high carbon fly ash mixed with the adsorbing AEA (SR) gives very high FI, both in "standard" and "short" procedures. These FIs (104-193) are even higher than the highest Foam Indices among the reviewed data presented in Table 2. Table 3 also shows that the "short" procedure reduces the FI for the adsorbing AEA compared to the "standard" procedure. That is, foaming is obtained with less AEA (and lower number of repeated shaking) by adding a lot of AEA at once, instead of many small droplets over long time.

Table 4 shows that the adsorption of AEA on high-carbon ash has a time-dependent effect on foaming, since the foam disappears within an hour (i.e., bad foam stability) and additional drops of AEA are needed to regain stable foam. Table 3 shows that the low-carbon fly ash gives a much lower FI, both in the standard and short procedures with AEA SR, though FI is still a bit high compared to the lowest FI values reviewed and shown in Table 2. From Table 4, it is seen that there is a time-dependent effect for this AEA-FA combination too, since the foam was not stable for an hour, but could be regained after additional AEA was added. The increase in FI from "short" to "long" procedure due to adsorption, and the new FIs, are seen in *italics* in Tables 3 and 4. Most additional AEA is needed on the high-carbon fly ash: *48* µL/g, whereas additional *4.8* µL/g is needed on the low-carbon fly ash.

Tables 3 and 4 show that the non-adsorbing AEAs (SOS, NVR) on high-carbon fly ash have comparably low Foam Indices: 40 and 32 µL/g in the standard FI. SOS was also run in the "short" and "long" procedures and showed no time dependency, since there was little/no difference in FI. (The reduction in FI from 40 to 36 for SOS on high carbon fly ash in table 3 when going from "standard" to "short" is within the error of the experiment). Furthermore, the foam remained stable over 1 hour (see bold numbers for the non-adsorbing SOS). Finally, we see from Table 3 that the non-adsorbing SOS with the low-carbon fly ash has the lowest FI of all combinations, with FI values comparable to the lowest values in Table 2.

The time dependency of the adsorption had a clear effect on increasing the foam index, since less AEA became available for foaming. The standard procedure, with drop-wise addition and shaking at regular intervals, took 3 hours to obtain stable foam for the adsorbing SR on high carbon fly ash. This reduced to only 3 minutes to obtain stable foam in the short procedure and then increased to (60+13) minutes in the "long" procedure. For the adsorbing SR on low-carbon fly ash, the "standard" test took 12 minutes, while the "short" test took 6 minutes and then the "long" test took (60+14) minutes. Apparently, adsorption went on for quite some time, since the time to regain foam by drop-wise addition after 1 hour took 13 – 14 minutes, whereas the "short" procedure could create a lot of unstable foam when adding a lot of AEA quickly. For the non-adsorbing SOS on high-carbon fly ash, the test time was 50 minutes in the standard FI test, reducing to 5 minutes in the short test and then remaining stable for an hour (i.e., no increase of FI in the "long" test).

5.   CONCLUSIONS

The Foam Index (FI) test measures the amount of AEA needed per gram of binder so that the foam remains stable. FI is performed by adding drops of AEA-solution, shaking and observing foam stability. It is useful for assessing the AEA dosage needed for different binder compositions. Furthermore it has given good correlation to air entrainment in concrete within three studies, even though the mechanisms of foaming and concrete air entrainment are quite different.

Combining FI-tests and adsorption studies with TGA and NMR showed high FI for AEA that adsorbs (SR – Saponified Rosin), both on high-carbon FA (FI very high = 193 mL/g) and on low-carbon FA (FI quite high = 18.4 mL/g). Furthermore, the FI was low for AEA that does not adsorb (FI = 4.8 for SOS – Synthetic Olefin Sulfonate) on low carbon FA. FI was high for AEAs that do not adsorb (FI = 40 and 32 for SOS and NVR - Neutralized Vinsol Resin) on high-carbon FA.

The FI and the foam stability were affected by the time dependency of the adsorption, since for the AEA that adsorbed (SR) a short test-time procedure with large AEA addition always reduced the FI compared to the slower standard dropwise addition of AEA. Furthermore, a long test time always increased FI compared to the short test procedure; that is, AEA must be added to retrieve the foam lost after 1 h waiting. FI is practically unaffected by time for the AEA that does not adsorb (SOS), as the foam remains stable after 1h.

The relation between adsorption and foaming and the expected relation to concrete air entrainment, as well as the changes of the AEA caused by adsorption that were observed by NMR, warrant more studies in search of robust air entrainment for fly ash concrete.

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