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Replacement of the foam index test with surface tension measurements

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Abstract

The foam index test is the method usually employed to determine the degree of fly ash interference with air entrainment agents in concrete. The test involves the use of commercial air-entraining agents (AEAs) and visual observation of foam stability. These facts reduce the reproducibility of the test, because commercially available AEAs vary in strength, and the criteria for foam stability are operator dependent. Therefore, it is of interest to develop a reproducible method, which is able to determine the fly ash quality with respect to air entrainment in concrete. This paper presents efforts toward the development of a new method based on dynamic surface tension measurements, using the bubble pressure method, on filtrate from a fly ash and cement suspension. A pure surfactant is added to the suspension as a substitute for a commercial AEA. The new method and the foam index test have been compared on fly ashes acquired from power plants in Denmark and the U.S. The results reveal a good relationship between the two methods, but the new method requires further work before a finished procedure is accomplished. Finally, it has been shown that changes in temperature affect both test methods.

Keywords: Fly ash; Concrete; Air entrainment; Foam index; Surface tension

1. Introduction

To increase the workability of freshly mixed concrete and improve its resistance to damage from freezing and thawing in hardened stage, air is entrained into the concrete paste [1]. The air entrainment is enhanced by addition of air-entraining agents (AEAs) and these are typically aqueous mixtures of ionic and non-ionic surfactants, which adsorb strongly to the air–water and air–cement interface, thus distributing the air as sub millimeter bubbles throughout the concrete [2].

Portland cement used in the concrete manufacturing is often partly replaced by fly ash produced at high temperature in pulverized coal combustion. Due to the pozzolanic properties of fly ash, i.e. its capability to react with water and calcium hydroxide from cement and form cementitious products at ambient temperature [3], it is found to be a very suitable additive in the production of concrete. Improvements like lower water/gas permeability and increased strength are obtained [3–5] as well as lower production price of the concrete [6].

Fly ash is reported to interfere with air entrainment in concrete [3,7–9] and the implementation of low-NO_x combustion technologies in recent years has increased the problem [10]. The residual carbon in fly ash is believed to adsorb the AEAs in the concrete mixture, which lead to lower amounts of entrained air [11–13]. Compared to the other compounds of fly ash, the unburned carbon provides active adsorption sites for the hydrophobic part of the surfactant. Studies have shown that not only the amount of unburned carbon is related with the adsorption of AEAs, but properties such as accessible surface area and surface chemistry have also been argued to influence the adsorption capacity [11,13].

Fly ash quality, with respect to interference with air entrainment in concrete, is commonly determined by a simple titration method known as the foam index test [14], which has been proven to correlate well with the air content in mortar [15] or the AEA requirements in mortar [16]. The latter study is repeated in [17]. The test involves addition of a commercial AEA to a fly ash and cement suspension followed by shaking.

Abbreviations: AEA, air entraining agent; CMC, critical micelle concentration; FI, foam index; SD, standard deviation; SDBS, sodium dodecyl benzene sulfonate; ST, surface tension.

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The AEA leads to foam formation on top of the liquid surface, which initially behaves in an unstable manner. At the endpoint of the test, the active adsorption sites of the unburned carbon are "saturated". Further addition of surfactants contributes to the foam formation and it eventually becomes stable [18]. The amount of AEA required to obtain a stable foam depends on the fly ash quality. A poor quality fly ash has a tendency to show high AEA requirements, i.e. more AEA is needed to obtain stable foam.

The foam index test is not a standardized method. Hence it is difficult to compare results between different laboratories. Problems like various laboratory procedures and different chemical nature, aqueous concentrations and aging of commercial AEA utilized in the tests have been discussed by Külaots et al. [18]. Moreover, testing time [13,19] and the individual operator criteria for foam stability may affect the result. Manz et al. [6] recommended to modify the foam index test and to develop spectrophotometric methods in order to determine the adsorption behavior of carbon in fly ash. However, attempts to correlate UV–Visual spectroscopic measurements with the foam index test, have been without success [19]. It was suggested that soluble ions provided in various amounts from the fly ash interfered with the measurements. In another publication, aqueous solutions of different pure surfactants were successfully tested against two commercial AEAs according to the foam index procedure [18]. The two commercial AEAs showed quite different strength (3 times), but correlated well with each other when being compared on different ashes. The results indicated that similar behavior would be observed on a wide range of commercial AEAs. Moreover, it was argued that application of pure surfactants in the test would avoid the varying properties of commercial AEAs [18] and thus, it was recommended to apply the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) in further work (Fig. 1). Sensitivity of SDBS toward effects from water soluble compounds in the fly ash tended to be lower compared with commercial AEAs, and it was discussed how problems with aging were avoided by using SDBS. In addition, SDBS is utilized as AEA in lightweight concrete [20] and its use has been reported in other publications [21,22]. In the present work, it was decided to proceed with SDBS as an AEA substitute. Other benefits from using SDBS, is that its chemical nature makes it suitable for quantitative analysis using UV–absorbance; the absorbance maximum of alkylbenzensulfonates is about 223 nm [23].

In this paper, further steps are taken to completely avoid operator dependent observations of foam stability, and instead replace it with a measuring technique based on surface tension measurements. In summary, the goal is to develop a reproducible method which is able to detect even small differences in fly ash adsorption capacity of surfactants. Foaming behavior and foam film stability is influenced by the liquid phase composition such as ionic strength [18,24], insoluble compounds [18], pH [18,25] and concentration of surface active compounds [24,26]. Again, many of these parameters affect the surface tension of the liquid phase [27] and a relationship between foam stability and surface tension has been shown [28].

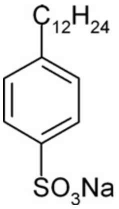

Fig. 1. Molecular structure of SDBS, MW=348.48 g/mol.

2. Experimental

2.1. Materials

The method developed was evaluated on nine fly ash samples, activated carbon and pure cement. Furthermore, a carbon free fly ash sample was included in the test. The carbon was removed by heating the ash for 2 h at 740 °C in atmospheric air. The fly ashes were produced from combustion of bituminous coal or anthracites and are acquired from Danish and U.S. power plants. Their carbon contents range from 2.2 to 30.6 wt.% and was determined using an ELTRA model CS-800 apparatus. The activated carbon powder (Norit GSX 100 mesh size) came from Lancaster Synthesis GmbH. A commercial Portland cement (Rapid) with a fineness of 444 m^2/kg and 2.4 wt.% loss of ignition was included in the test. The cement was provided by Aalborg Portland A/S. Particle size measurements were carried out in dry state using a Malvern Mastersizer. SDBS purchased from Sigma-Aldrich Chemie GmbH was used in the surface tension measurements. The critical micelle concentration (CMC) of SDBS was determined by isothermal titration calorimetry on a MicroCal ITC-2000 calorimeter [29]. The AEA used in the foam index test was Conplast 316 AEA. According to the manufacturer (Fosroc), it is a "chloride free air-entraining admixture on a synergistic blend of naturally occurring surfactants".

2.2. Foam index test

The procedure for the foam index test is similar to that which others have proposed [17,18,30]. 2 g of fly ash, 8 g of Portland cement, and 25 ml of deionized water were poured into a cylindrical glass vessel being 6 cm in diameter, which was capped and shaken on a vortex shaker for 1 min. A 5 vol.% aqueous solution of AEA was added in small aliquot amounts (20 μl) from a diluter and the vessel was shaken for another 15 s. The foam was observed for stability, i.e. defined as no bursting of bubbles within 30 s. In case the foam was unstable, more AEA was added, and the procedure was repeated until the foam remained stable. The foam index test was carried out at least two times on each ash sample, and the reported value is the average. The actual foam index value is obtained by subtracting from the measured value the value of a blank performed on a pure cement, and it is given in milliliters per 2 g of fly ash or normalized to the carbon content in the ash, also known as the specific foam index.

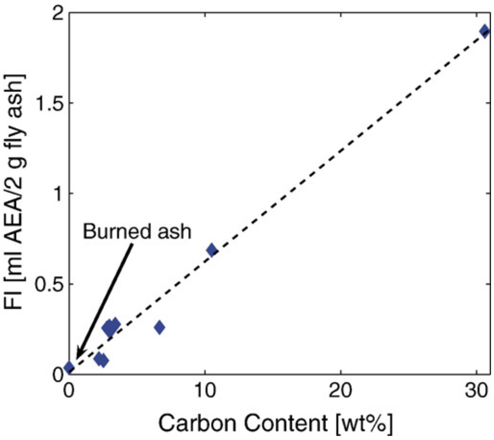

Fig. 2. Foam index values compared with carbon content of fly ash.

2.3. Surface tension measurements

The sample preparation differs only slightly from the foam index test. The test involved placing 2 g of fly ash and 8 g of cement in a plastic beaker. 25 ml of an aqueous SDBS solution (0.5–1.0 g/l) was introduced into the beaker, and it was shaken for 5–30 min during the optimizing process of the test and 10 min in the final experiments. The suspension was centrifuged for 1 min followed by filtration of the supernatant (0.45 µm cellulose acetate filter). Surface tension measurements based on the maximum bubble pressure method were carried out on the filtrate using a SITA tensiometer model science line t60. The samples were prepared two times unless otherwise stated, and the reported surface tension is an average of at least five subsequent measurements. In case the difference between the double determinations was higher than 1 mN/m, the sample was prepared a third time and an average of all three samples is reported. The minimum of five subsequent surface tension measurements was chosen as compromise between reducing the standard error and keeping the testing time low. Cement was included in the sample preparation, in order to achieve mixture conditions corresponding to the foam index test and to reduce interference from soluble ions provided by the fly ash as suggested by others [19].

The maximum bubble pressure method is a fast and reliable way to determine the dynamic surface tension [31]. Compared with static methods, the surface age in dynamic methods is too short to obtain equilibrium tension where no further surfactants diffuse to the surface [27]. A capillary is introduced into the solution and bubbles are grown on the tip. The pressure difference required in the bubble formation is proportional to the surface tension of the solution [32]. Due to the dynamic behavior of the test method, increasing bubble lifetimes will cause lower measured surface tensions [31]. Thus, method development included determination of optimal bubble lifetime.

2.4. UV-measurements

Initially, the maximum absorbance of SDBS in H_2O and in aqueous filtrate containing electrolytes, such as Ca^{++} and Mg^{++} [19,33], provided from a cement and fly ash suspension, was determined. The calibration curve of SDBS was constructed from various concentrations of SDBS in H_2O up to 0.1 g/l, which was the limit for the absorbance measurements. Different SDBS concentrations in 5, 10 and 20 vol.% solutions of filtrate from a cement and fly ash suspension were prepared to study any deviation from the calibration curve based on SDBS in H_2O. All measurements were corrected by a background measurement on diluted filtrate alone corresponding to the applied solutions (5 to 20 vol.%). Pharmacia Biotec Ultraspec 3000 was used as spectrophotometer.

The fly ash and cement samples were prepared similar to the surface tension measurements and the SDBS solution was added in 0.6 and 1.8 g/l concentrations. In addition, a background was prepared from adding pure water to the fly ash and cement. The resulting filtrates were diluted before the UV-measurements to get below the limit of electrolyte interference, which was determined from the calibration curve of SDBS in pure water and the SDBS in the filtrate solutions. 0.6 g/l SDBS solutions were also prepared in pure filtrates from cement and cement/fly ash samples and in the same filtrates diluted two times with water. The solutions were allowed to stand for 3 days to ensure equilibrium. The resulting precipitates were removed by filtering and the filtrates were diluted for the UV-measurements. The measured concentrations of SDBS in the filtrates were used to estimate the precipitated fraction of SDBS.

3. Results and discussion

3.1. Foam index values

Foam index values from which the blank value of pure cement has been subtracted and specific foam index values are shown in Figs. 2 and 3, respectively. The results support the trends shown in past publications [13,14,21]: the foam index tends to increase with the fly ash carbon content (Fig. 2); but the unburned carbon in fly ash can show quite different adsorption capacities of AEAs (Fig. 3). The foam index value of the burned ash further proves how the residual carbon contributes to increased AEA requirements. The foam index went from 0.26 ml/2 g fly ash (2.8 wt.% carbon) to 0.04 ml/2 g fly ash

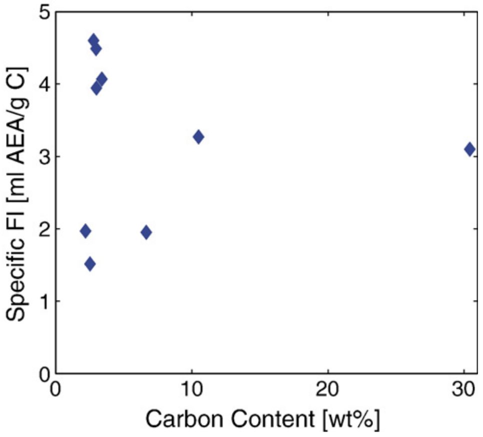

Fig. 3. Foam index values normalized into ml AEA program of carbon in the ashes.

when the carbon was removed, which is similar to what others have observed [18].

Attempts to carry out the foam index test with SDBS as AEA substitute were done in the present work as in the study by Külaots et al. [18]. For unknown reasons, stable foams corresponding to the endpoint of the test could not be obtained in the experiments. The amount of foam increased with adding SDBS, but the bubbles were still bursting within the 30 s. Further efforts to solve this problem were not considered.

3.2. Optimizing surface tension measurements

Applied bubble lifetime and initial concentration of SDBS in the surface tension measurements are based on the experimental data presented in Figs. 4–6, where the fly ash and cement suspensions have incubated with SDBS in different concentrations for 10 min. The results are presented as single determinations. The consequence of having an initial concentration of SDBS on 0.5 g/l is revealed in Fig. 4, where only a minor difference in the measured dynamic surface tension can be detected in a wide span of bubble lifetime between two high carbon ashes. It appears as if both ashes have adsorbed most of the added surfactant, making it difficult to measure any difference in their adsorption capacity. On the other hand, an initial concentration of SDBS on 1.0 g/l (Fig. 5) leads to similar dynamic surface tension measurements of both cement and a low carbon ash, indicating that the amount of surfactant adsorbed by the fly ash is low compared to the remaining SDBS in the solution. The CMC of SDBS may explain this observation. Normal surfactant behavior is observed below the CMC, i.e. surfactants are found as monomers and the concentration relates to the surface tension [27]. Above the CMC the hydrophobic part of the surfactant interacts with other surfactants leading to micelle formation, where only the hydrophilic part is in contact with the aqueous phase. The micelles are not surface active and hence will not contribute to changes in surface tension. Published CMC values of SDBS in H_2O range from 0.52 g/l (temperature not provided) [34] to 1.88 g/l (22 °C) [35]. The CMC was in this work determined to approximately 0.24 g/l at 30 °C in H_2O. It is noted, that the CMC for ionic surfactants typically is lowered by the presence of electrolytes [27] but this issue was not further addressed in the present work. In any case, dynamic measurement methods are suitable for concentrations above the CMC opposite to static methods [31]. This was demonstrated on different surface active compounds at temperatures ranging from 30 to 80 °C [31].

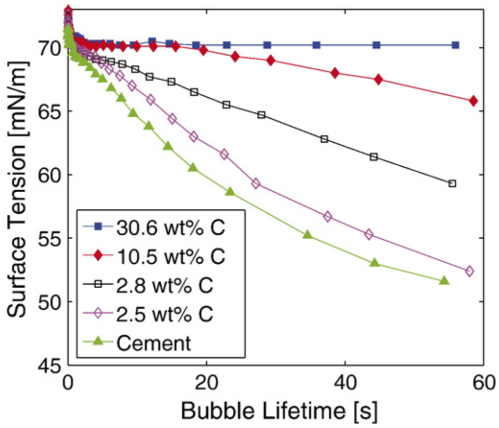

Fig. 4. Dynamic surface tension versus bubble lifetime at 0.5 g SDBS/l in initial concentration. The incubation time between surfactants and fly ash/cement was 10 min.

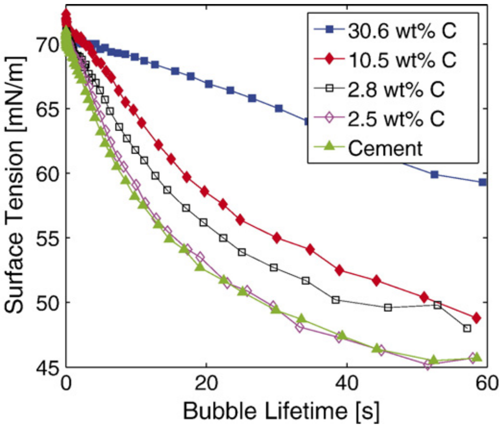

Fig. 5. Dynamic surface tension compared with bubble lifetime at 1 g SDBS/l in initial concentration. The incubation time between surfactants and fly ash/cement was 10 min.

Addition of a 0.6 g/l SDBS solution gives a detectable difference between both low and high carbon ashes as shown in Fig. 6. It is evident, how utilization of a short bubble lifetime leads to similar surface tension results. Equilibrium between surfactants in the solution and at the surface are not obtained due to a short age of the bubble surface (short adsorption time of the surfactants) and the surface tension of the pure solvent is measured [31], being water in this case (72.3 mN/m at 23 °C). At high bubble lifetime, the surfactants move toward equilibrium and the surface tension is lowered. Hence, any variation in surface tension between the samples can be detected. On the other hand, the difference in surface tension between the samples appears not to increase substantially when a bubble lifetime above 20 s is applied, making it a reasonable choice in further measurements. Moreover, testing time will significantly

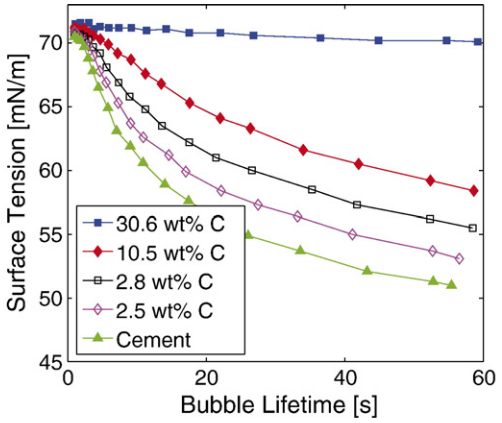

Fig. 6. Dynamic surface tension versus bubble lifetime at initial SDBS-concentration on 0.6 g/l and 10 min in incubation time.

be extended with higher bubble lifetime because the results are based on the average of at least five measurements.

Surface tension measurements of two ashes plotted against the time between surfactant addition to the cement/fly ash sample and centrifuging of the mixture are displayed in Fig. 7, where the surface tension is observed to increase with time. The intention was to achieve equilibrium conditions, where no further surfactant adsorption took place and in this way, minimize the influence from incubation time on the measurements. The laboratory data show a continuous increase in surface tension with incubation time likely due to a decrease in surface active compounds, in which the latter support the results reported by others [13,19,36]. Freeman et al. [13] found that more AEA was required to achieve the endpoint of the foam index test with increasing testing time. The observed dynamics in this method are expressed by a higher surface tension with longer incubation time. In fact, the equilibrium is not reached within the 30 min, which is at least 20 min more than the time of the foam index test. Diffusion limitations of surfactants into the carbon particle [13,36] and formation of insoluble compounds due to the presence of CO_2 in the atmosphere [19] may be the reasons. In terms of the latter, it has been suggested that carbonic acid, produced from dissolving of atmospheric CO_2, leads to formation of insoluble free surfactant acids [19], and this was to some extent supported from the present experiments as well: initially during optimizing of the bubble pressure method, the filtrate surface was in contact with atmospheric air resulting in formation of a white precipitate on top of the liquid surface during testing time. This was prevented by conducting the surface tension measurements under nitrogen (only the results in Figs. 4 and 5 are conducted in atmospheric air). It is noted that others have shown a leveling off in AEA adsorption within 10 min, when conducting the experiments under nitrogen [19] or in a closed system [21]. The results of the present experiments, showing a continuous increase in surface tension with time of samples mixed in a closed system, contradict these studies. Incubation time was chosen to 10 min corresponding to the usual time of a single foam index test. The time is sufficient to detect difference in AEA requirements of the foam index test and keeps the testing time of the present method low.

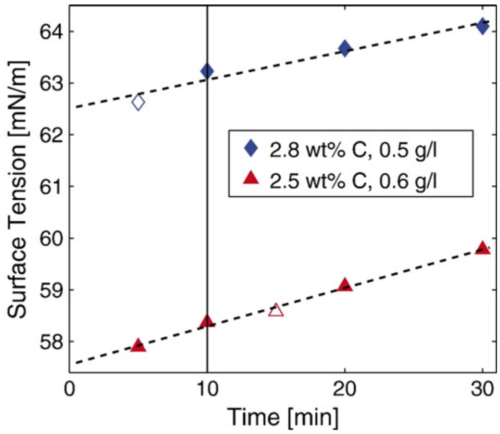

Fig. 7. Surface tension determined at 21.6–22.0 °C (2.8 wt.% C) and 22.1–22.5 °C (2.5 wt.% C) compared with incubation time. The unfilled and filled markers represent single and double determinations respectively. Initial concentration of SDBS = 0.5–0.6 g/l. The solid vertical line corresponds to the usual time of the foam index test.

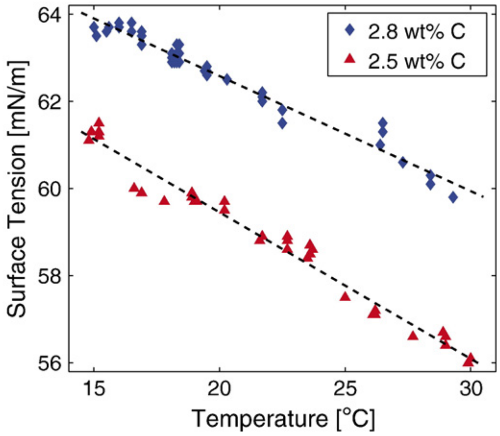

Fig. 8. Surface tension and temperature measured on the filtrate from two fly ashes (each sample prepared once). 0.6 g/l SDBS in initial concentration and 10 min in incubation time.

The sensitivity of the surface tension toward the temperature of filtrate prepared from two fly ashes is seen in Fig. 8. The surface tension drops by 0.26 mN/(m °C) (2.8 wt.% C) and 0.34 mN/(m °C) (2.5 wt.% C) with increasing temperature and the linear decrease is consistent with the literature [27]. To avoid temperature dependency, the filtrate was placed in water bath during the surface tension measurements in order to work close to isothermal conditions within the same experimental series. It is evident that future steps in the method development could include implementation of temperature-correlation. Considering the high temperature sensitivity of the surface tension, it was questioned whether the temperature affects the foam index values as well. The subject is addressed in Section 3.5.

3.3. *Comparison of surface tension measurements and foam index*

Fig. 9 presents surface tension measurements on filtrate from cement/fly ash samples compared with their respective foam

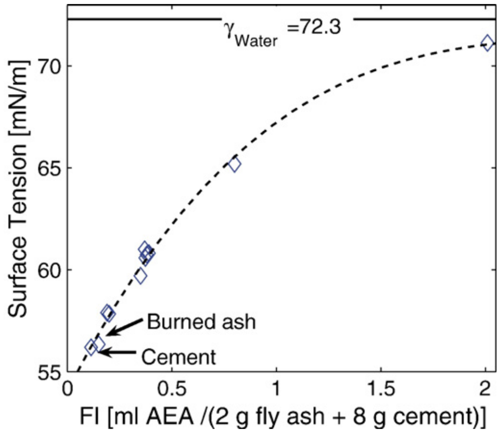

Fig. 9. Surface tension of filtrate compared with foam index. The temperature of the filtrate was between 22.7–22.9 °C. 0.6 g/l SDBS in initial concentration and 10 min in incubation time.

index values. Cement is included in the evaluation and therefore, the reported foam index values have not had the cement (blank) value subtracted. To reduce the influence of the previously described interfering parameters affecting the foam index test, all measurements have been conducted by the same operator in one batch within the same day. The results display a good correlation between the two methods. Increasing foam index of a fly ash corresponds to higher adsorptivity toward surfactants as previously discussed. In the surface tension method, the concentration of surfactants in the aqueous phase is reduced by the adsorption, leading to higher surface tensions. The correlation appears to be linear within lower adsorption capacities of fly ashes (0–6.7 wt.% C). At higher adsorption capacities, the new test meets its limit under the applied conditions. It is obvious, that surface tension values cannot exceed the surface tension of the pure liquid (γ_{water}). Thus, ashes with high adsorption capacities will result in filtrates with low surfactant concentrations and show surface tensions close to pure water, making it difficult to detect any variance in their adsorption capacity. Measurements on activated carbon which are highly AEA adsorptive (FI > 14 ml/2 g C) confirm this behavior. The surface tension was measured as 71.9 mN/m, indicating that the surfactants have been exhausted from the supernatant fluid completely. Therefore, in order to detect any difference in surface tension of high adsorption ashes, a greater initial concentration of SDBS must be applied. However, as Fig. 4 shows, the difference between ashes with lower adsorption capacities will then be more difficult to detect (Section 3.2).

3.4. Evaluation of surface tension method

The overall repeatability of the method was tested by preparing the same two ashes at least 10 times followed by surface tension determinations and the results are provided in Table 1. Given the small surface tension difference of 2.7 mN/m between the two ashes, which shows quite different foam index values, the variation of the test is found to be high, making it difficult to detect small differences in adsorption capacities of ashes. Nevertheless, their 95% confidence intervals are not overlapping and this indicates a significant difference in their adsorption capacities for surfactants. The variation may be caused by the bubble tensiometer and varying ash sample properties. The former is stated to have repeatability error of 0.5 mN/m. This was checked on a 0.2 g/l SDBS solution divided into 6 samples. Surface tension was measured on each sample and was found to be 37.5 mN/m with 0.04 mN/m in standard deviation at 22.1–22.4 °C. The results do not explain the poor repeatability. Particle size measurements on repeated ash and cement samples, taken from the same beaker, did not indicate any variation in the size distribution, which might have influenced the varying adsorption behavior as well. Of course, variation in surface area and porosity of the residual carbon is not revealed from the particle size distribution.

Table 1
Repeatability of two ashes, SD is the calculated standard deviation

Carbon	[wt.%]	2.8	2.5
FI	[ml AEA]	0.38	0.20
No. of measures		10	11
ST	[mN/m]	61.5	58.8
SD	[mN/m]	0.51	0.48
Range	[mN/m]	60.7–62.4	58.1–59.5
Temperature	[°C]	23.4–23.6	21.0–21.4

Adsorption time = 10 min and initial concentration of SDBS = 0.6 g/l. The foam index is given in ml AEA/(2 g fly ash + 8 g cement).

Steps to increase the repeatability and sensitivity of the test can be taken in two directions, i.e. lower the variation within single samples and expand the surface tension scale. We suggest replacing cement with a solution containing a known electrolyte composition and alkalinity corresponding to what a cement suspension would provide. This will, as cement does, minimize the influence of various soluble ions provided by the fly ash [19] but prevent the interference of varying cement properties. As described in Section 3.2 a white precipitate was formed on the liquid surface when conducting the surface tension measurements under atmospheric air indicating that CO_2 was dissolved in the filtrate. The observation is in contradiction with what others have proposed [18], that the alkaline “buffer” provided by the electrolytes eliminate the influence from CO_2 dissolution. To increase the surface tension scale, it is suggested to change surfactant. As results below reveal (Section 3.6), a large fraction of SDBS precipitates due to formation of insoluble compounds with the electrolytes in the solution, as observed by others [19]. Surfactants of non-ionic character may avoid this problem, since they are less inclined to salt out [23], and they increase the solubility of metal anionic surfactant salts [37]. Higher sensitivity may also be obtained by changing the initial concentration of surfactant. For instance, if the investigated ashes are known to be within a certain adsorption capacity region, then the initial surfactant concentration could be optimized in order to detect small variations in that particular region.

A fundamental difference between this new method and the foam index test is the procedure for adding surfactants. In the foam index test, the surfactants are added stepwise until a stable foam is obtained, whereas in the present method, the surfactants are added in one step at the beginning of the test followed by surface tension measurements after a given incubation time. In order to obtain the same order of magnitude between results of different ashes by the two methods, the surface tension method could be based on same principle as the foam index test. For instance, the surfactants could be added continuously to a stirred mixture of cement and fly ash while the surface tension of the aqueous phase is measured. The endpoint of the test will be when it reaches a defined surface tension. The rate of adding surfactants are believed to have a significant impact on the result as in the foam index test [18] and will require further attention.

3.5. Temperature effects on foam index values

The relationship between temperature and surface tension inspired us to conduct the foam index test at two temperatures corresponding to conditions in a room and in a cold outdoor environment. The experimental data are presented in Fig. 10. It appears as if less AEA is required to obtain a stable foam at

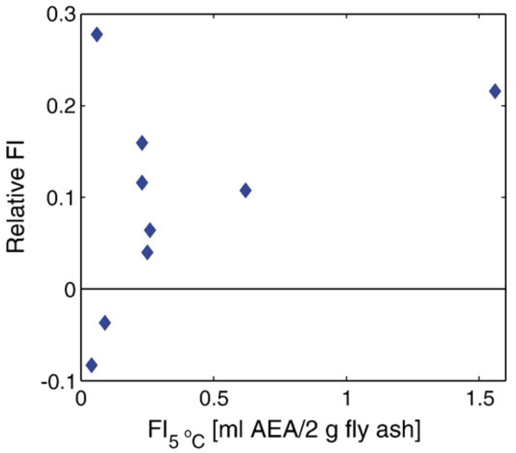

Fig. 10. Relative difference between foam index carried out at 5±1 °C and 27±1 °C $\left(\text{Relative FI} = \frac{FI_{27\,°C} - FI_{5\,°C}}{FI_{5\,°C}}\right)$.

lower temperatures. Only in case of very low foam index values (burned ash and fly ash with 2.2 wt.% carbon content), the opposite trend is observed, which is believed to be due to that lower values can be presented with greater uncertainties. Temperature effect on foam stability has been investigated by others [38,39] and a similar trend was observed. Decreasing temperature gives rise to higher viscosities of the liquid phase and this lowers the drainage of the foam film. The increased viscosity may partly be caused by micelle formation, which usually is enhanced at lower temperatures [27]. Thus, the lifetime of the foam is prolonged and less AEA is required to obtain a stable foam. Furthermore, it is possible that diffusion of AEA molecules into the carbon particles is reduced due to lower temperatures (which will apply for the surface tension method as well). The results provide additional problems in standardizing the foam index test. Varying testing temperatures due to location, season or even heating of sample by hand give rise to a poor comparability with earlier results.

3.6. UV-measurements

In the search of an explanation for the low difference in surface tension measurements between ashes having high difference in foam index values, the concentration of SDBS in the cement and fly ash filtrates was determined by UV-measurements.

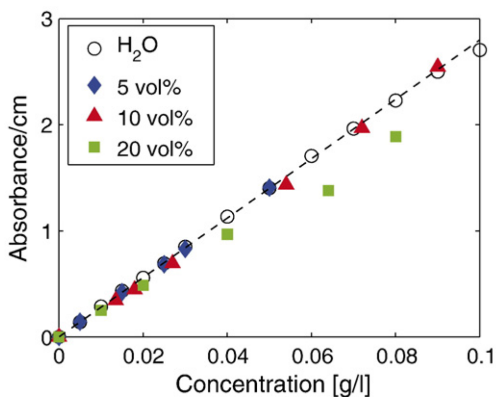

Fig. 11. Calibration curve of SDBS in 0–20 vol.% aqueous solutions of cement and fly ash filtrate ($C_{SDBS}=0.036 \cdot ABS$).

Table 2
UV-measurements at 223 nm of cement and fly ash sample (single determinations)

Sample	$C_{SDBS,0}$ [g/l]	ABS/cm	C_{SDBS} [g/l]
Cement	0.6	0.132	$4.71 \cdot 10^{-2}$
Fly ash	0.6	0.120	$4.28 \cdot 10^{-2}$
Cement	1.8	0.275	$9.82 \cdot 10^{-2}$
Fly ash	1.8	0.252	$8.99 \cdot 10^{-2}$

The absorbance (ABS) is measured on a 10 times diluted sample. The concentration of SDBS is reported as the added solution ($C_{SDBS,0}$) and in the resulting filtrate (C_{SDBS}), which has been recalculated to original sample.

The maximum absorbance of SDBS dissolved in H_2O was determined to be at 222.3 nm and about 0.5 nm higher when prepared in filtrate containing electrolytes from cement and fly ash. Both samples were mixed in a closed system. The calibration curve obtained at 223 nm in Fig. 11 shows linearity up to 0.09 g/l. Good correlation between absorbance and SDBS concentration was obtained in 5–10 vol.% solutions of filtrate, even though visible insoluble compounds, presumably being precipitated calcium surfactant salts [33], had formed in the 10 vol.% solution. No visible insoluble compounds were formed in the 5 vol.% solution. The good linearity could not be obtained at 20 vol.% solution, which from a visual comparison had the highest turbidity. Therefore, the following UV-measurement was conducted on filtrate diluted to 10 vol.% in water. Results from background measurements showed that the electrolytes only had a small contribution to the absorbance at 223 nm (0.04 at 20 vol.% solution).

Table 2 provides the laboratory data from adding two different concentrations of SDBS to pure cement and a cement and fly ash sample. Table 1 summarizes the properties of the fly ash (2.8 wt.% carbon), while for cement the foam index has been found to be 0.12 ml AEA/8 g cement and the surface tension was measured to be 56.2 mN/m. In order to be below the limit of electrolyte interference, all resulting filtrates were diluted 10 times before UV-measurements as described above. The results show that 7–8% of the initial added SDBS concentration on 0.6 g/l remains dissolved in the filtrate and only 5% when adding 1.8 g/l SDBS solution. Considering the three times higher foam index of the examined fly ash compared with pure cement, the difference in remaining SDBS concentration

Table 3
Concentration of SDBS in pure filtrate (1:1) and in filtrate diluted two times (1:2) from a cement and fly ash solution

Sample	Filtrate	ABS/cm	C_{SDBS}[g/1]
Cement	1:1	0.640	$1.14 \cdot 10^{-1}$
Cement/fly ash	1:1	0.672	$1.20 \cdot 10^{-1}$
Cement	1:2	0.256	$9.14 \cdot 10^{-2}$
Cement/fly ash	1:2	0.295	$1.05 \cdot 10^{-1}$

Amount of SDBS has been added corresponding to 0.6 g/l in concentration. The absorbance was measured on 5 (1:2) or 10 (1:1) times diluted samples to be below electrolyte interference, and the concentrations of SDBS are recalculated to original sample.

between the filtrates of the two samples is low for both initial concentrations of SDBS (approximately 9% of the mean value). The observation is believed to be directly related with the low difference in measured surface tension between the two samples.

The low amounts of dissolved SDBS in the filtrate may partly be explained by the results in Table 3, which shows the attempts to prepare a 0.6 g/l SDBS solution in pure filtrate from cement and fly ash and in the same filtrate diluted two times with water. Recalculating absorbance measurements into concentrations shows that approximately 80–85 wt.% of the added SDBS is not dissolved in the aqueous phase, probably due to formation of insoluble calcium surfactant salts [19]. Others have found similar trend with other surfactants too [33]. This implies that only 15–20 wt.% of SDBS will be left to detect difference in adsorption behavior of the ashes. The sensitivity of the surfactant toward the ions coming from cement may be reduced by applying a non-ionic surfactant in the surface tension measurements as discussed in Section 3.4.

As a final comment, we believe that the parameters affecting the foam stability (described in Section 1), may complicate the development of spectroscopic assays. Such methods will only report a surfactant concentration and not an overall contribution to foam stability.

4. Conclusions

The commonly employed foam index test, which determines fly ash quality for concrete utilization, has been compared with a new method based on surface tension measurements, using the bubble pressure method. The comparison has been done on pure cement, nine fly ash samples and a carbon free ash sample and good relationship was accomplished between the two methods. The new method takes away the individual operator criterion on foam stability, making the test easier to standardize. Moreover, the test can be based on using a pure surfactant instead of an air-entraining agent, where commercial products show variation in chemical nature and concentrations.

To summarize the method we have:

- Added a standard surfactant solution to a mixture of cement and fly ash.
- Allowed it to incubate under shaking for 10 min, followed by centrifugation and filtration.
- Measured the surface tension of the filtrate with the bubble pressure method at a fixed temperature and bubble lifetime.

The described method is at present stage not a finished procedure, but needs further work to fulfill our goal of having a reproducible method, which is able to detect small differences in fly ash adsorption capacities of surfactants. Improvements for the method have been suggested, which should be tested in the further work. The applied anionic surfactant was found to be very sensitive to the electrolytes provided from the cement and fly ash. We suggest testing non-ionic surfactants instead, which are less sensitive to form insoluble calcium surfactant salts. In order to prevent the interference of varying cement properties in the test, while still reducing the influence of the various soluble ions provided by the fly ash, we suggest testing if the applied cement can be replaced with a well defined electrolyte solution. Effort should also be put into testing if the protocol of adding surfactants should be changed.

Finally it has been shown that changes in temperature affect the foam index test.

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