

Fly Ash-Carbon Effects on Concrete Air Entrainment: Fundamental Studies on their Origin and Chemical Mitigation

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ABSTRACT

This paper describes the results of an investigation designed to gain further insight into interactions between FA-carbon and air-entraining surfactants, and the way in which these interactions impact on the stability of air voids dispersed in cement paste. The influence of different forms of powdered carbon and other hydrophobic particles on paste air entrainment and foam generation with a typical air-entraining surfactant was investigated. As might be expected, the various types of hydrophobic particles induced an important reduction of paste air content and foam stability.

To elucidate the origin of these observations, the adsorption of the surfactant (sodium dodecylbenzenesulfonate, DDBS) by various hydrophobic particles, and the wetting behaviour of these particles in water and surfactant solutions were investigated. The results confirm that surfactant adsorption contributes to reduce paste air entrainment and foam stability. Additionally, the results demonstrate that fine hydrophobic particles can also influence paste air or foam stability through a disruptive action of the particles directly on the surfactant film. These observations provided important clues for mitigating the influence of FA-carbon on concrete air entrainment through 'sacrificial admixtures'. Observations on surfactant adsorption and wetting behaviour of hydrophobic particles in the presence of a model 'sacrificial admixture' yield a comprehensive description of the mode of action of these admixtures.

INTRODUCTION

The negative impact that fly ash can have on concrete air entrainment is well documented¹⁻⁵, generally through studies relating air entrainment and the amount of unburned carbon remaining in the FA (LOI). However, important deviations from the air-LOI relationship have forced more detailed investigations of the interaction between the surfactants used as air entraining admixtures (AEA) with the FA-carbon, or with other components of fresh concrete².

Considering the conditions under which FA is formed, the properties of the residual FA-carbon should be similar to those of a partially oxidized coke¹ comprising isotropic (amorphous) and anisotropic (crystalline) carbon and inertinite²; properties of this residual carbon may thus be similar to those of an activated carbon, or of a soot (carbon black)^{4,5}. From this analogy, the influence of FA-carbon on air entrainment in concrete is usually attributed to the interaction of the carbonaceous material with the air-entraining surfactant (AEA), i.e., adsorption onto the carbon reducing the AEA available to promote the formation of a stable air void network^{1,2,4}. The relationship between surfactant adsorption and air entrainment reduction was demonstrated in FA-cement pastes in several recent reports^{6,7} and further discussed in a previous paper in this conference⁸. On the other hand, it was also found recently that some materials, although having low surfactant absorption capacity, also had negative impact on air entrainment⁹.

To further elucidate the role of FA-carbon on concrete air entrainment, an investigation was undertaken on the influence of various forms of carbon and other types of particles on air entrainment in cement pastes and on surfactant foam stability. A parallel investigation of surfactant adsorption by the different types of particles was also carried out, as well as quantitative measurements of the wetting behaviour of these particles (contact angle, wetting rates).

The same experimental strategy was pursued to investigate the mode of action of a new class of admixtures which can neutralize the detrimental influence of FA-carbon on concrete air entrainment. These admixtures, labelled 'sacrificial admixtures'^{7,10} are not air-entraining in themselves and were initially thought to perform carbon 'masking' simply through preferential adsorption, i.e., adsorbing preferentially onto FA-carbon, releasing the AEA to perform its intended function.

The combined results of the present study provide a more accurate description of the influence of FA-carbon on surfactant films at the solution/air interface of an air bubble, or at the paste/air interface of a concrete air void. The results also provide a more detailed understanding of the role of 'sacrificial admixtures' which, although not intrinsically air-entraining, can efficiently neutralize the effect of FA-carbon on concrete air entrainment.

EXPERIMENTAL

Materials

A GU (type I) portland cement from St Laurent, Québec, Canada was used for all cement pastes of the present study; its composition was given in a previous report⁸. As fine particulate materials used in most of the experiments, i.e., paste air entrainment, foam generation, surfactant adsorption and wetting, four types of carbon particles were selected and five other types of solids. The composition, source and some key properties of these materials are presented in Table 1 and Table 2.

The origin and chemical composition of the surfactant (Na-dodecylbenzenesulfonate, DDBS) and the model sacrificial agent (ethyleneglycolphenylether, EGPE) investigated are presented in Table 3; the latter also gives the critical micelle concentration (CMC) of DDBS. The CMC is the solution concentration at which the surfactant molecules undergo spontaneous aggregation, the more active surfactants forming micelles more readily, i.e., at lower surfactant concentration.

Foam column volume measurements

A simple protocol was used¹¹ to evaluate the volume and stability of surfactant foams and the influence of various types of particles or the model sacrificial agent on these foams. In the protocol used, a foam column is generated by flowing air through a fritted glass disc fitted at the bottom of a glass column (1m H*4.7cm D); the latter is also equipped with three valves to control air flow, draining and washing.

Table 1: Designation and origin of particulate materials used

Product	Name	Code	Source
Activated carbon		AC	Norit
Carbon black	Printex 55	CB2	Degussa
Carbon black	Printex L6	CB3	Degussa
Graphite powder		G	Fisher
Teflon		Teflon	Aldrich
CaCO ₃ treated ⁽¹⁾	Omycarb FT	CaCO ₃ T	OMYA
CaCO ₃ non-treated ⁽²⁾	Omycarb F	CaCO ₃ NT	OMYA
Talc treated	Nicron 665	Talc T	Luzenac
Talc non-treated	Cimpact 699	Talc NT	Luzenac

⁽¹⁾ Contains 1% Magnesium carbonate + 1.1% Stearic acid

⁽²⁾ Contains 1% Magnesium carbonate

Table 2: Selected properties of carbon and other materials used.

Code	BET ⁽¹⁾ (m ² /g)	Size ^{(1) (2)} (μm)	Density ⁽¹⁾ (g/ml)	COT ⁽³⁾ (mg/100g solid)	Surface energy Fowkes (mN*m ⁻¹)
AC	450	21.6	2.11	0	67
CB2	89	(0.025)	1.83	0	53
CB3	240	(0.018)	1.88	0	65
G	22.5	5.0	2.35	0	75
Teflon	21.5	1.0 (1.0)	(2)	12	18
CaCO ₃ T	5.9 (5.5)	2.0 (1.4)	2.84 (2.7)	17	54
CaCO ₃ NT	10.9 (7)	2.0 (1.4)	2.60 (2.7)	14	57
Talc T	32.2	3.0 (1.2)	2.64 (2.8)	0	50
Talc NT	34.6	3.0 (1.5)	2.80 (2.8)	0	46

⁽¹⁾ in parenthesis: from manufacturer

⁽²⁾ d₅₀ median diameter

⁽³⁾ in filtrate of 2% solid in 0.03N NaOH pH 12.5

Table 3: Properties of surfactant and sacrificial agent investigated.

Product	Code	MW	Formula	CMC (mM)	Source
Na-Dodecyl benzene sulfonate	DDBS	348.48	C ₁₂ H ₂₅ C ₆ H ₄ SO ₃ Na	1.2 (25°C) 1.19 (75°C) ⁽¹⁾	TCl
Ethylene glycol phenyl ether	EGPE	138.2	C ₆ H ₅ OCH ₂ CH ₂ OH	na	Aldrich

⁽¹⁾ Ref. ¹²

Surfactant or sacrificial agent solutions (30mM) were prepared in 0.03N NaOH (pH 12.5). Air volume measurements were performed by weighing precisely in an 800mL clean and dry beaker, 3g of DDBS solution, a given amount of EGPE solution and distilled water to give a total of 271g. A given amount of particles was then added; the quantity of solids was selected as to have approximately the same total surface area for all solids. The suspension was homogenized for 20min with a high speed mixer, then transferred into the column (near the bottom) using a long neck glass funnel; the beaker and funnel were then rinsed with 250g of distilled water to ensure complete transfer of all components into the column.

The nitrogen pressure was adjusted at 15psi and the flow meter (Cole Palmer, graphite ball, scale 0-150) was set at position 30 for adequate gas flow; the same settings were retained for all experiments. Measurements of the heights of the foam and of the liquid were performed at 1, 3, 5 and 15 min then the foam volume was calculated.

Physico-chemical properties of solid particles

The size distribution was determined using a MALVERN SIZER 2000, Malvern Instruments Inc. The solid particles (80mg) were dispersed in a 50ml solution of 0.1%wt dispersant using an ultrasonic probe (650W) at 80% intensity for 10min, cycling: 20sec ON and 10sec OFF. The beaker was in placed in a cooling jacket containing ice to minimize heating from the ultrasonic energy.

The nitrogen BET specific surface area was determined using a Quantachrome Autosorb-1. The tube containing about 0.02 to 0.10 g of powder was under vacuum (12h at 60.0°C to obtain a final pressure of 10^{-3} Torr or less).

The specific gravity of the various solid particles was determined at 25.0 °C using Le Chatelier flask (pycnometer) with kerosene as a solvent.

The amount of organic material which can be leached from the various solids investigated in NaOH 0.03N was determined by TOC measurements on a Shimadzu, Model TOC 5000A carbon analyzer. The measurements were performed on the filtrate from 2%wt suspension of the solids after shaking for 30min, centrifugation and filtration (0.45µM).

Preparation of pastes

Pastes were prepared by 1 min rapid hand mixing of the solids (400 g of cement and carbon or other particles) and liquid (water and surfactant and/or other additives), followed by intense stirring at room temperature during 2 min using a hand-held mixer (BRAUN model MR400) positioned at 6.3 cm from the bottom of the mixing vessel. Details of the equipment and experimental protocol were reported previously^{6,8}.

The water-cement ratio (W/C) was chosen as 0.46 in order to obtain a mini-slump¹³ spread diameter of 110 ± 5 mm after 10 min with the control paste (without additives). In the presence of additives, mini-slump was measured but not further adjusted.

Paste air measurements

The total volume of air entrained in pastes was determined from density measurements as described earlier^{6,8}. To evaluate the rate of air loss, measurements were performed at 30 minute intervals (6, 36 and 66 min), each time after 1 min gentle hand mixing. Validation of the method against mortar and concrete air measurements was documented earlier⁶.

Adsorption of surfactant and sacrificial agent on carbon and other particles

Surfactant or sacrificial agent (SA) solutions were prepared in 0.03N NaOH (pH 12.5) and adsorption measurements were performed by UV spectroscopy as follows. An amount of solid, chosen to maintain a relatively constant total surface area with the different solids, was suspended in 400ml of the 0.03N NaOH solution; the latter was homogenized as required to achieve optimal dispersion for 20min. Keeping under agitation, 40g of this suspension was transferred into a 50ml polypropylene tube and the desired amount of DDBS or/and EGPE solution was added. The suspension was allowed to equilibrate for 30min under moderate shaking, then filtered (0.45 μm), or centrifuged (13000 g) to recover a clear filtrate, i.e., the carbon black particles are too fine to be filtered out efficiently. The residual surfactant or sacrificial agent in the filtrate was determined by UV absorption.

Contact angle measurements

In order to determine the wetting behaviour of the different solids, contact angle measurements were performed on a 'bed' of particles prepared as follows. A nonconductive double sided adhesive tape (SPI Supplies) was affixed onto a clean microscope glass slide. The adhesion surface was then gently pressed onto a bed of the powdered solid; the excess powder was lightly tapped-off and the surface homogeneity was verified under a magnifying glass. If required, the procedure was repeated until a uniform, well-bonded layer of particle was obtained. Contact angle measurements on these particle layers were performed with selected solvents and solutions using a First Ten Angström, Model FTA 200 instrument; liquid drops were deposited on the particle layer via a syringe delivery system equipped with a 20 gauge needle. Using the instrument camera, drops were placed on the best surface available.

For particle wetting studies in the presence of the surfactant, the model sacrificial agent, or both, the following solutions were used and referenced to deionised water: DDBS 0.5mM, EGPE 2.0mM and mixture of DDBS 0.5mM and EGPE 2.0mM prepared in NaOH 0.03N solution.

Surface energy measurements

To assess the surface energy of the various particles, contact angle measurements were also performed on layers of particles with various solvents, namely, water, glycerol, di-iodomethane, ethyleneglycol, benzylalcohol and isopropanol having surface tension values between 72 and 23 dyne.cm^{-1} . The results for water and di-iodomethane

were used to calculate the surface energy of the solids according to the Fowkes method¹⁴⁻¹⁶.

RESULTS AND DISCUSSION

The data presented below are grouped according to the type of system or property examined: air entrainment, foam volume generation, adsorption and wetting. In each case, we report successively observations with the AEA (sodium dodecylbenzene sulfonate, DDBS) and with the model sacrificial agent, SA (ethyleneglycolphenyl ether, EGPE). The combined influences of DDBS and EGPE on the property or system examined are then described and discussed.

Characterization of carbon and other particles

The properties of the carbon and other particulate materials determined in this work are collected in Table 2. Most of the particles examined have diameters in the micron range, except for the activated carbon and some carbon black samples; the latter are respectively an order of magnitude larger and smaller than the others. This is partially reflected in the relative surface areas of the materials, except for activated carbon; the latter has a very high surface area which is largely due to its high porosity (internal surface area). The talc and graphite powders also yielded relatively large BET surface areas given their average diameters, suggesting they can have micro- or meso-porosity. The soluble organics which can be extracted from 2% particle slurries in NaOH 0.03N are either very low, or undetectable. At the levels detected, the soluble organics are highly unlikely to alter significantly the measurements described below.

Finally, the surface energy measurements performed on the different powdered-materials confirms that the Teflon particles are the most hydrophobic (lowest surface energy, $17\text{mN}\cdot\text{m}^{-1}$), whereas the graphite appears the least hydrophobic (surface energy, $67\text{mN}\cdot\text{m}^{-1}$), followed by activated carbon. The other materials exhibit comparable surface energies at $40\text{-}50\text{ mN}\cdot\text{m}^{-1}$.

Paste air studies

The influence of carbon particle on air entrainment in a cement paste is illustrated in Figure 1 showing paste air volume as function of AEA (DDBS) concentration. As is readily seen, the presence of small amounts of activated carbon dramatically increases the surfactant requirement to achieve a given air content, an effect widely attributed to the adsorption of the surfactant by the carbon particles^{2,3,10}.

Air entrapment/entrainment by particles

As a control test, the potential influence of the various types of particles on paste air content was determined in the absence of any surfactant. The results shown in Figure 2 indicate that most of the particles tested do not increase the amount of air entrapped in the cement paste; notable exceptions are Teflon particles. In the presence of significant

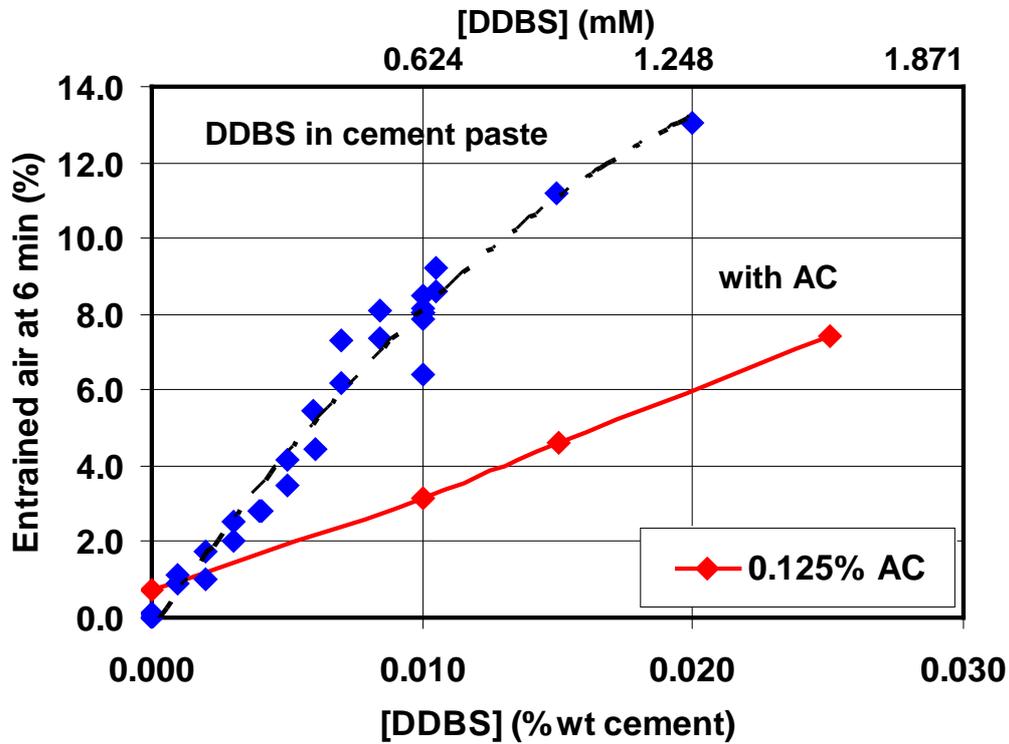


Figure 1: Upper curve: air entrained in a cement paste with increasing concentrations of Sodium Dodecylbenzene sulfonate (DDBS); lower curve, same in the presence of 0.125wt% added activated carbon. DDBS dosages: % by wt cement, or mM in batching water.

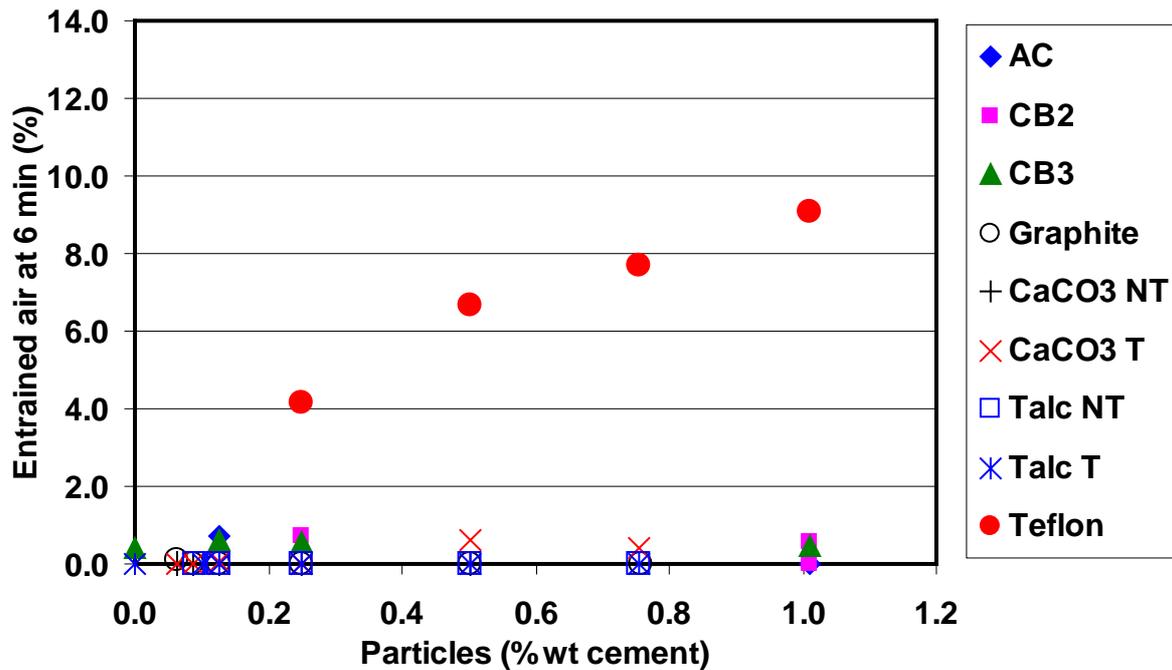


Figure 2: Air entrainment by particles without DDBS.

quantities of the latter ($> 0.1\text{wt}\%$ cement), considerable volumes of air can be entrained in the cement paste, much as with a surfactant. This observation most likely originates in the aggregation and spontaneous de-wetting of the hydrophobic particles, allowing air to remain entrapped in the particle cluster. Air entrapment observed recently in filtration dewatering of hydrophobic particle slurries had been attributed to this particular phenomena¹⁷.

Influence of particles on paste air entrainment

The paste air volumes entrained with $0.01\text{wt}\%$ DDBS in the presence of increasing quantities of various particle types is illustrated in Figure 3. Activated carbon and carbon black powders are seen to be very effective in depressing paste air entrainment by DDBS; however, all other materials tested also reduce DDBS air entrainment significantly, including Teflon which was shown to promote air entrapment on its own. Expressing particle contents in terms of the total surface area of the particles (rather than $\text{wt}\%$), the paste air data can be plotted as shown in Figure 4. Compared on the basis of relative particle surface areas, the hydrophobic particles (Teflon, carbon black) repress air entrainment more effectively than activated carbon or less hydrophobic particles (e.g. fine limestone particles reduce air entrainment, but only moderately).

The observed depression of paste air entrainment may be broadly attributed to surfactant adsorption by activated carbon or other particulate materials, as commonly noted in recent literature^{2,3}. As discussed in subsequent sections, however, the magnitude of air reduction does not follow the relative surfactant-binding ability of the different types of particles.

Influence of a model sacrificial agent (EGPE) on air entrainment

The effect of EGPE, introduced in the cement paste as a sacrificial admixture, is demonstrated in Figure 5. The latter first shows that, in cement paste containing $0.01\text{wt}\%$ DDBS, the addition of increasing dosages of EGPE leads to only minor increases in the paste air content.

On the other hand, in a paste containing the same DDBS dosage, and particles added in sufficient quantities to initially depress the entrained air to $2\text{-}3\text{vol}\%$, EGPE exerts a remarkable influence. With all types of particles, EGPE promotes substantial recovery of air entrainment. Interestingly, the recovery appears to reach a plateau at high EGPE dosages, indicating that the sacrificial agent could be added in excess quantities with minimal detrimental effect on air entrainment. These observations define and illustrate the concept and essential features of sacrificial agents: neutralize the effect of the carbon and allow the AEA agent to perform in a predictable way. The SA being neutral with respect to air entrainment, its dosage would not be critical beyond a minimum value.

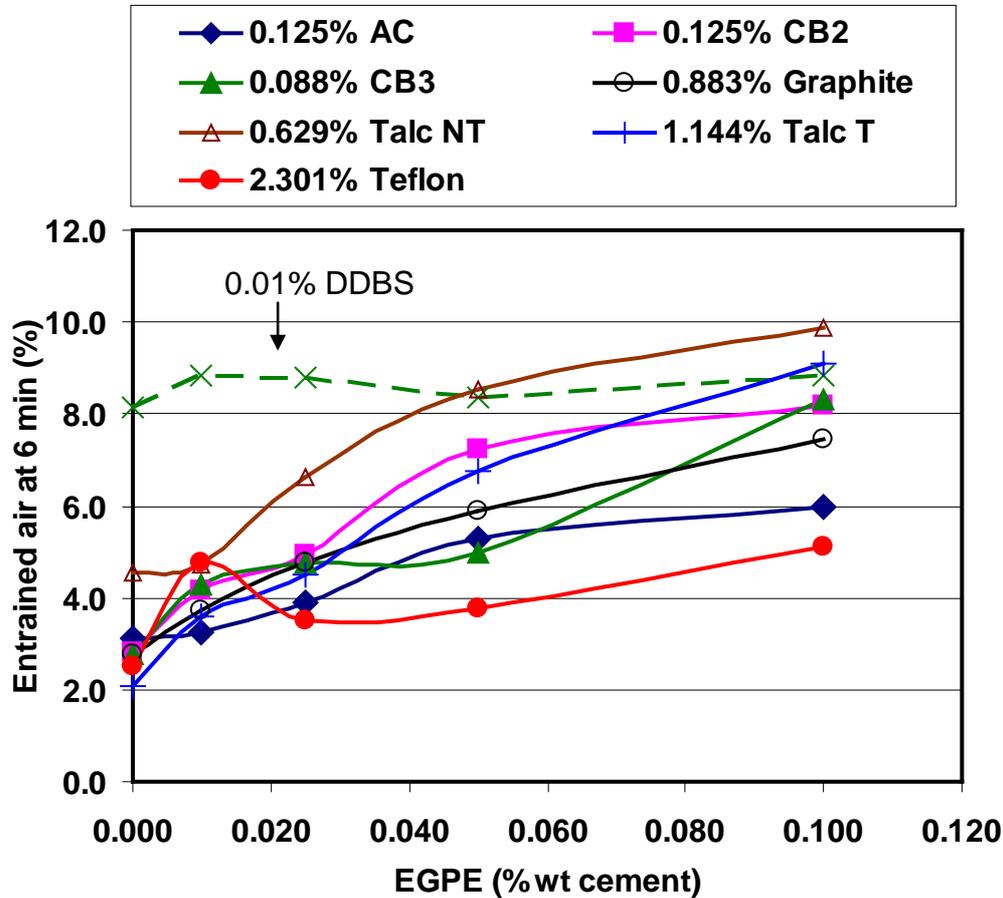


Figure 5: Influence of EGPE addition on recovery of air entrainment in cement pastes containing 0.01% DDBS and various types of solid particles; dotted line: control without particles.

Foam column studies

The foam volume generated in a column by a fixed DDBS dosage, under a constant air flow through a fritted glass is illustrated as function of time in Figure 6. In the presence of increasing amounts of activated carbon, the foam volume generated during a given period decreases substantially. This behaviour is shared by many types of hydrophobic particles examined here and is expected from prior investigations on the ‘defoaming’ properties of fine hydrophobic particles^{11,18-21}. At the highest amount of activated carbon tested, addition of small quantities of the sacrificial agent EGPE is seen to partially restore the foam volume (Figure 7). Very similar behaviours are observed with other particles, for example, carbon black for which the data is illustrated in Figure 8. In the latter cases, the foam volume recovery observed at the highest EGPE dosage is close to the initial value (graphite exhibits a very similar overall behaviour).

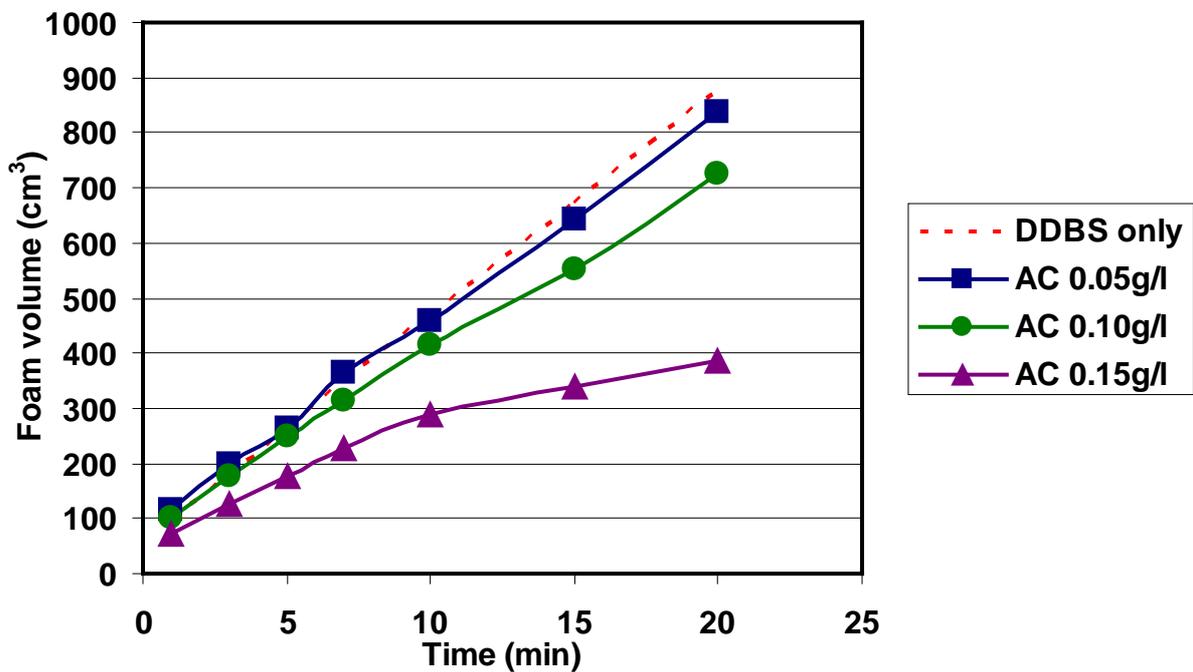


Figure 6: Influence of activated carbon (AC) content on column foam volume generated by 0.173mM DDBS.

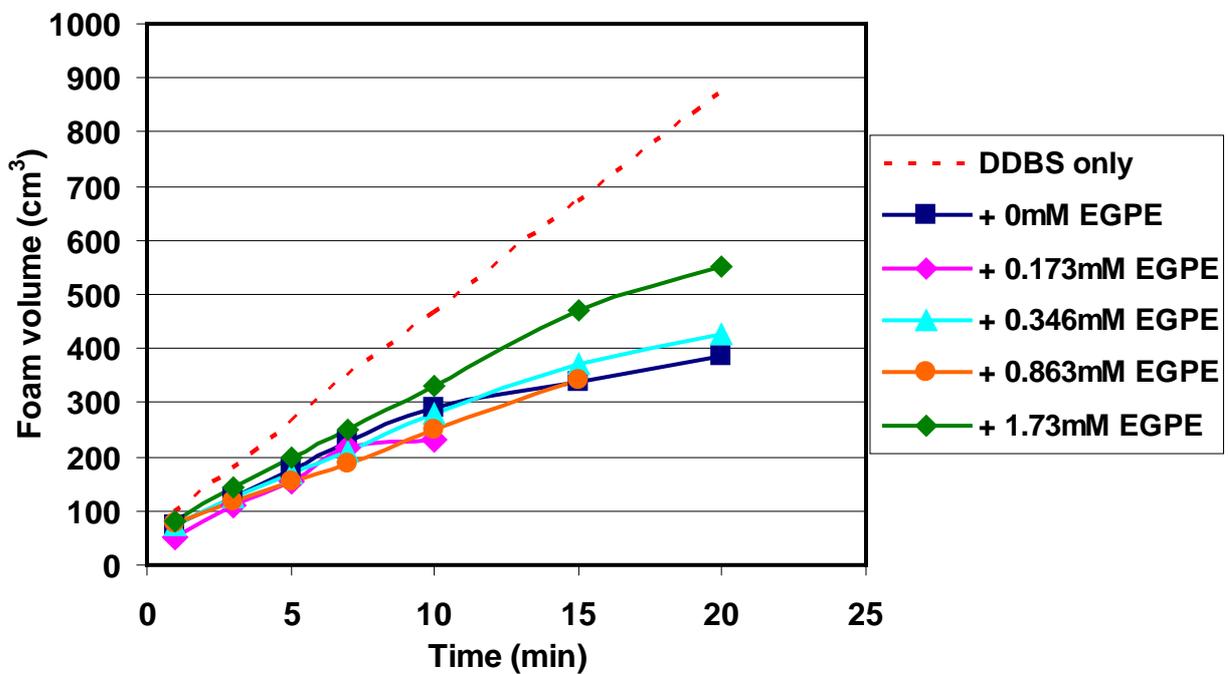


Figure 7: Effect of EGPE on column foam volume generated by 0.173mM DDBS in the presence of 0.15g/l activated carbon (AC).

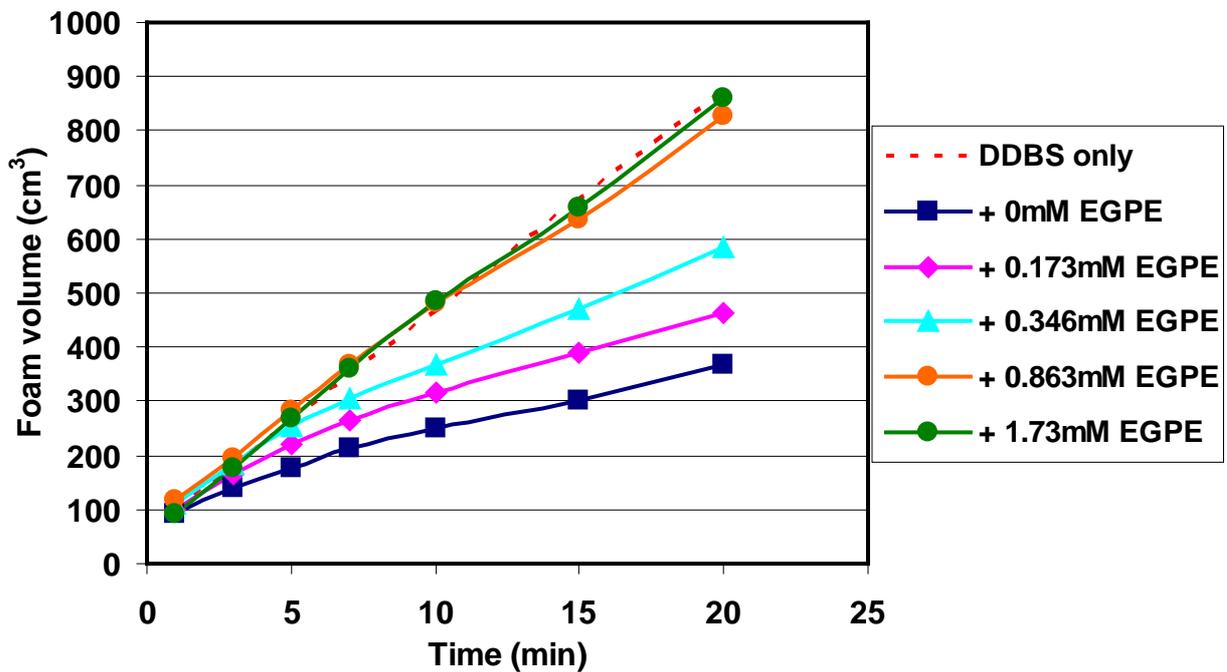


Figure 8: Effect of EGPE on column foam volume generated by 0.173mM DDBS in the presence of 0.10g/l carbon black #2 (CB2).

Foam measurement protocols have often been used for comparison of the relative efficiency of air-entraining agents, or relative evaluation of FA-carbon effects^{2,22}. In the present case, it is noteworthy that air foam generation and paste air entrainment follow closely similar trends, with respect to both the effects of hydrophobic particles and the influence of EGPE added as a sacrificial admixture. Again, it may be tempting to interpret the observations simply in terms of surfactant adsorption in both systems. Clearly, however, the structure and properties of a surfactant film in foams cannot be identical to those of a surfactant layer at the cement paste/air interface of an air void. The behaviours of these two systems are not expected to be related in a unique fashion, although they can be influenced by the same type of phenomena.

Adsorption studies

Adsorption of DDBS and EGPE various carbon particles

The adsorption of DDBS onto different types of carbon particles (activated carbon, carbon black and graphite) is illustrated in Figure 9. The adsorption data are reported as [milimoles of DDBS adsorbed/gram of solid]; when plotted as function of the equilibrium DDBS solution concentration, the data yield typical Langmuir-shaped curves in all cases. Corresponding data for EGPE adsorption yield a similar set of curves shown in Figure 10.

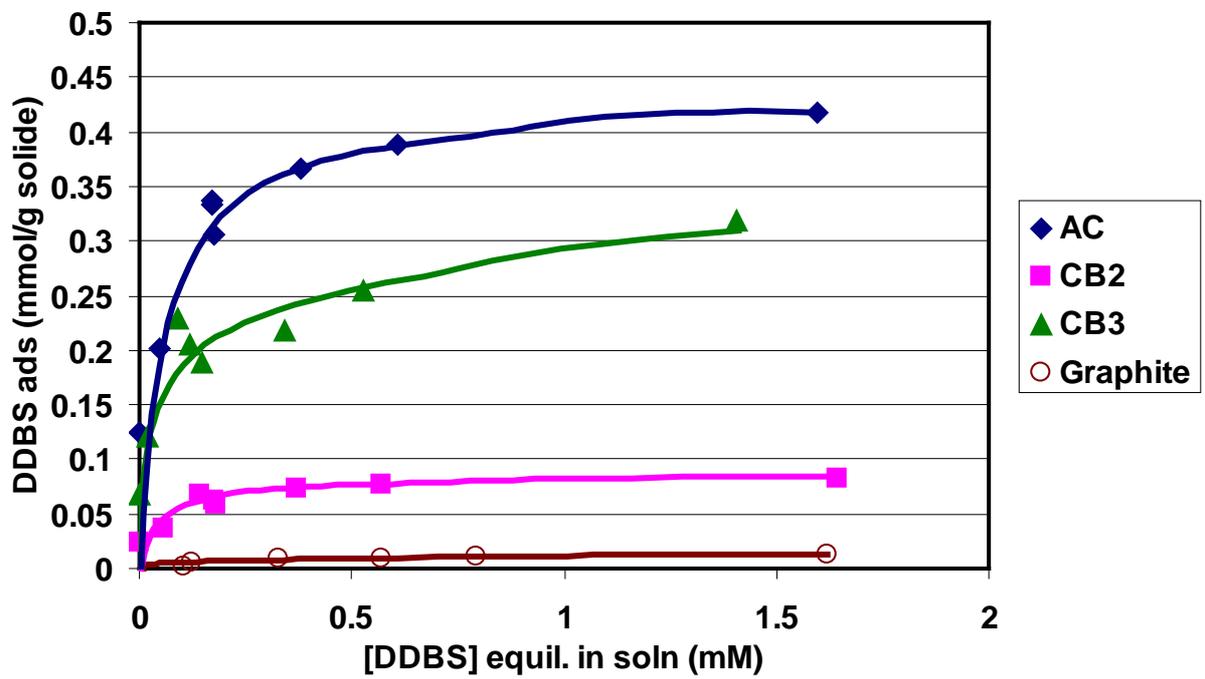


Figure 9: Adsorption of DDBS (mmol/g solid) on different types of solid particles

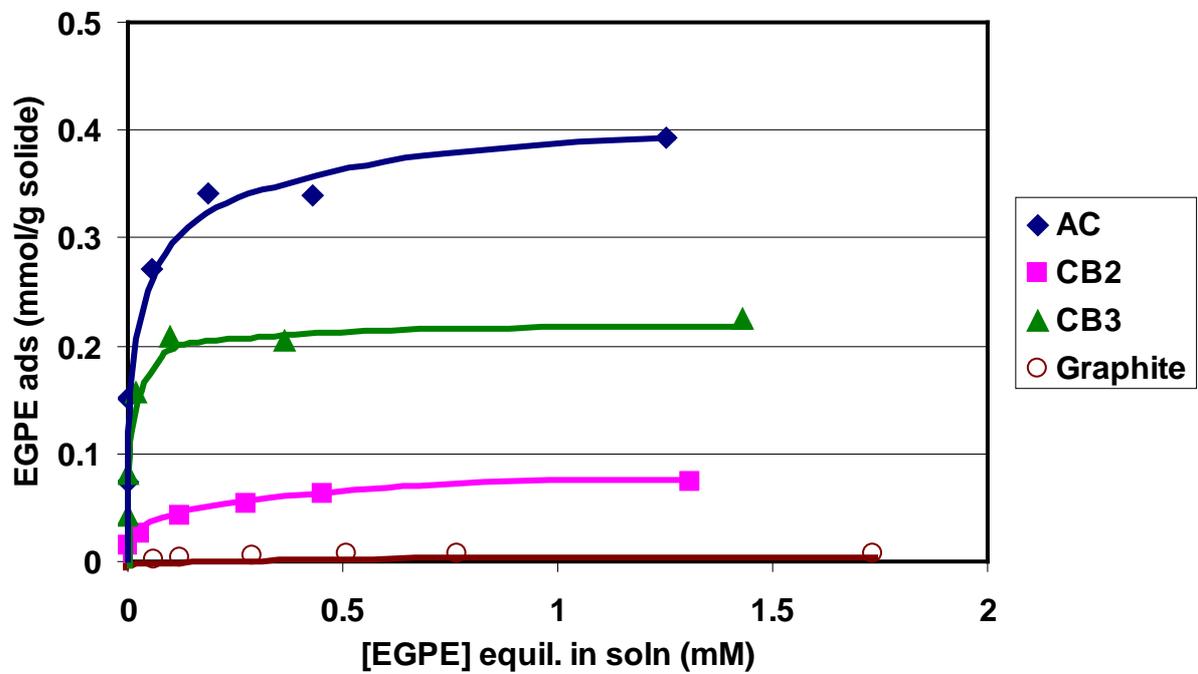


Figure 10: Adsorption of EGPE (mmol/g solid) on different solid particles

As is readily noted, the adsorption of DDBS and EGPE strongly depends on the type of carbon; part of these differences is, of course, related to the very different surface areas of the solids examined. However, the amounts (moles) adsorbed of DDBS and EGPE on a given type of carbon are of comparable magnitudes.

The parameters derived from this type of curve, namely, affinity constants and adsorption free energies were calculated and reported elsewhere⁹.

In an attempt to account for differences in the surface area of the various solids, an alternate representation of DDBS and EGPE adsorption behaviour is shown in Figures 11 and 12; the latter reports the adsorption data as [number of molecules/unit surface area (nm^2)], based on the N_2 BET surface area. As expected, normalization of the adsorption data to unit surface area reduces the spread of the calculated adsorption values with either DDBS or EGPE (it should of course be acknowledged that the N_2 -BET surface area might not adequately reflect the area accessible to the DDBS or EGPE molecules).

Comparing the BET-area normalized data, it is apparent that graphite adsorbs significantly less DDBS or EGPE than the other forms of carbon examined. With Teflon particles, the amount of surfactant or EGPE was not significantly outside the experimental uncertainty.

These results point to two significant issues. First, adsorption of DDBS and EGPE at comparable levels on all types of carbon materials suggests that competitive adsorption should be important (assuming the adsorption is reversible). Second, the lower adsorption capacity of graphite contrasts with its effectiveness in reducing air entrainment or foam stability, suggesting other contributing effects, as noted earlier.

Competitive DDBS/EGPE adsorption

Based upon the relative adsorption of the surfactant (DDBS) and the model sacrificial agent (EGPE), we may expect that, in a competitive adsorption situation, EGPE can displace DDBS from the adsorbing surface, and vice versa. The series of competitive adsorption data reported below does not entirely support this prediction.

To test the significance of competitive adsorption/displacement effects on the role of sacrificial admixtures, adsorption experiments were carried out for DDBS and EGPE alone at a fixed initial dosage (0.5mM); then the adsorption of each compound was measured in the presence of, first, an equal dosage of the other, and second, a dosage four times higher(2.0mM). The order of DDBS-EGPE addition was also varied to test for any irreversible adsorption effects. Figures 13 and 14 report the equilibrium adsorption data (mmol/g solid) derived from these experiments for activated carbon and two carbon black materials.

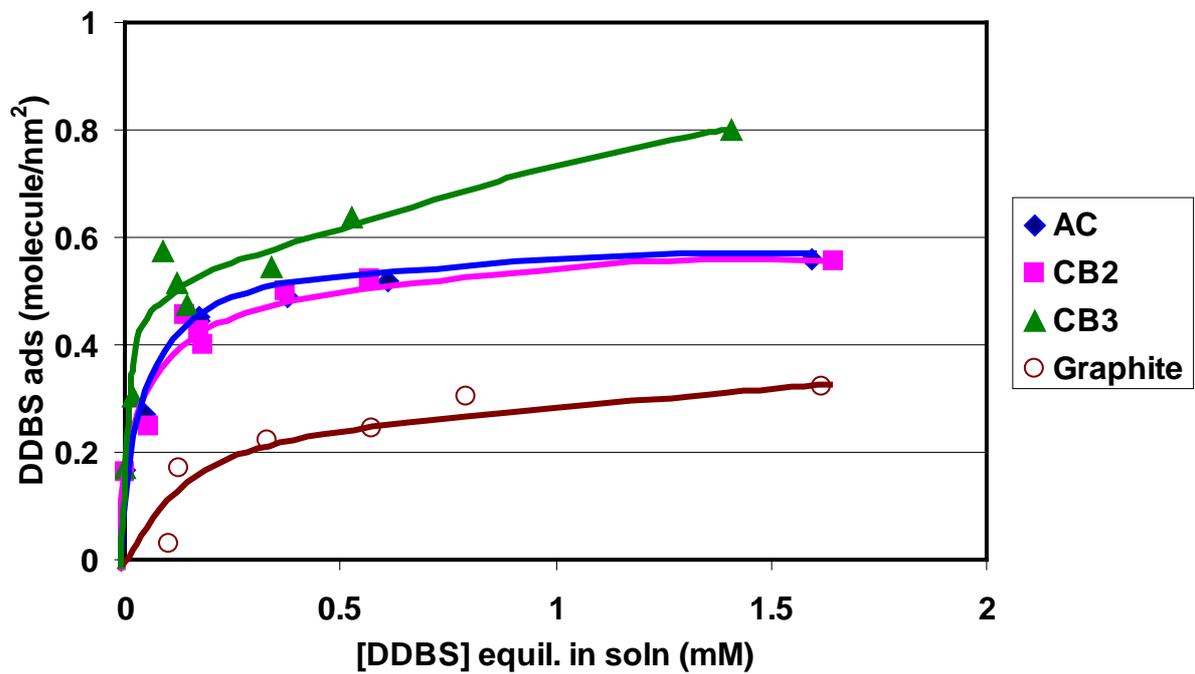


Figure 11: Adsorption of DDBS (molecules/nm²) on different solid particles

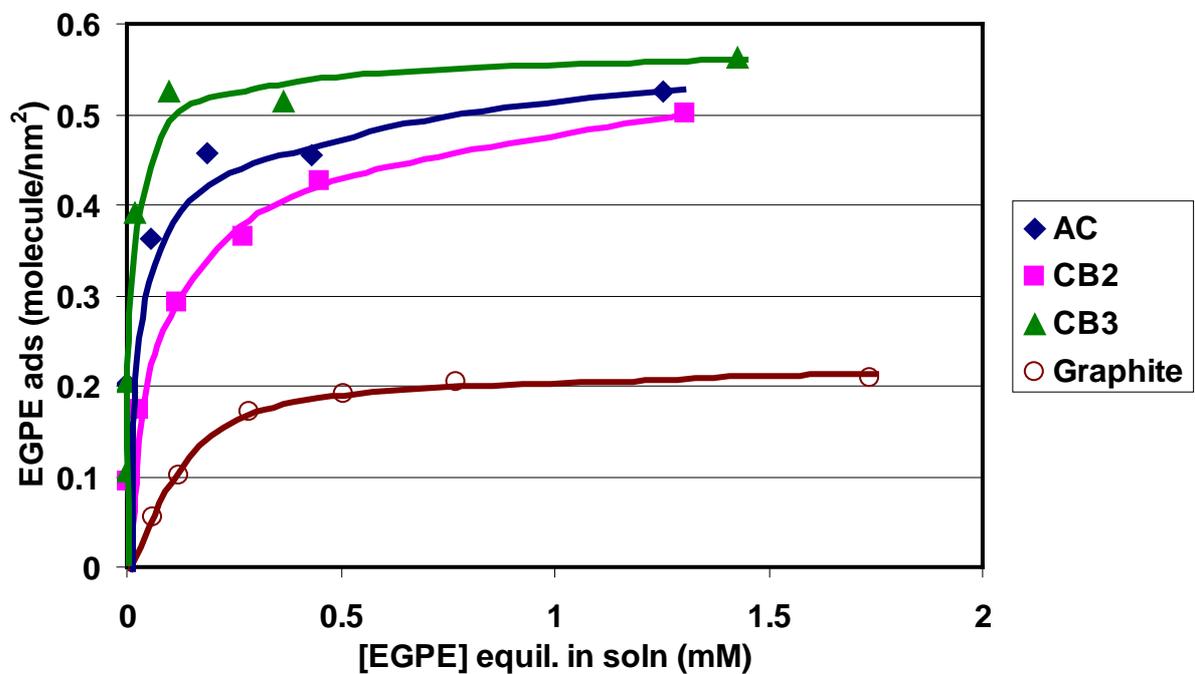


Figure 12: Adsorption of EGPE (molecules/nm²) on different solid particles

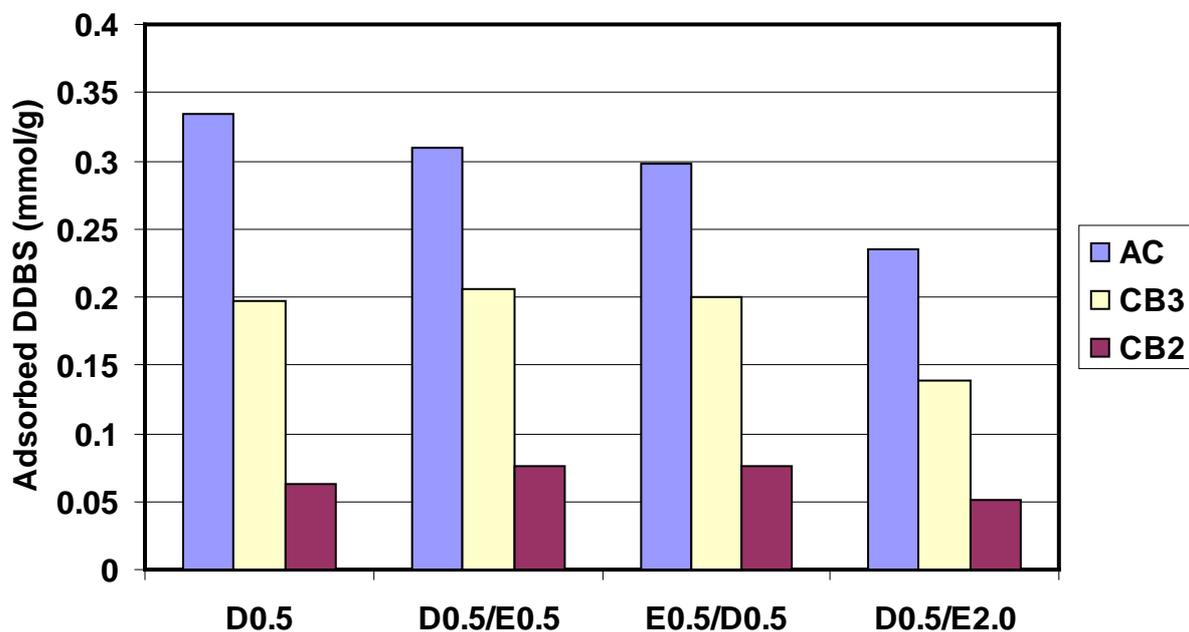


Figure 13: DDBS adsorption alone and in the presence of EGPE (E: EGPE; D: DDBS. Numbers refer to concentrations in mM).

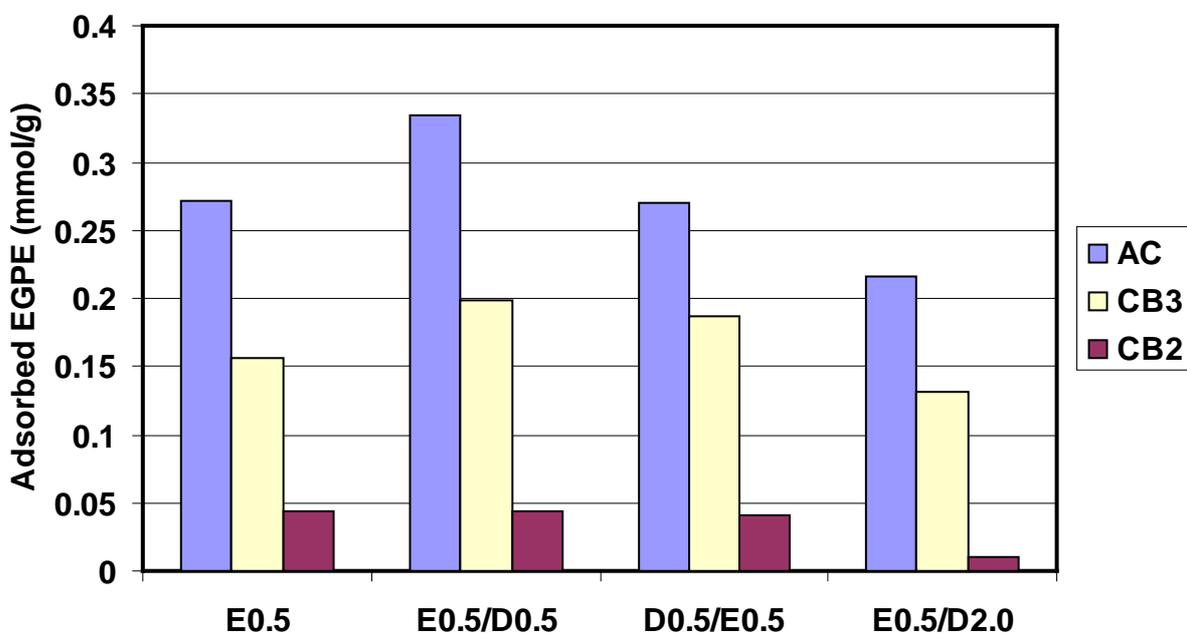


Figure 14: EGPE adsorption alone and in the presence of DDBS (E: EGPE; D: DDBS. Numbers refer to concentrations in mM).

Comparing DDBS adsorption data (Figure 13), it is immediately apparent that the presence of equal or 4x concentrations of EGPE has a rather weak effect on DDBS adsorption on all solids, while, introducing EGPE before or after DDBS (equal dosages) yields no significant difference in DDBS adsorption. The EGPE adsorption data yields a similar overall picture: marginal effect of DDBS on EGPE adsorption (except for CB2 with a 4x dosage of DDBS), and a slightly enhanced EGPE adsorption when the latter is added prior to addition of DDBS.

In the light of these observations, and inferences from paste air or foam volume measurements, it seems unlikely that sacrificial agents operate solely through competitive adsorption releasing the surfactant AEA into solution, i.e., as originally thought¹⁰.

Particle wetting behaviour

The wetting behaviour of various hydrophobic particles was examined through measurements of contact angles as function of time (0-60sec) with DDBS, EGPE and mixed DDBS-EGPE solutions. The conditions and dosages were selected similar to those used in competitive adsorption studies discussed above.

Part of the data obtained on the wetting behaviour of activated carbon is reported in Figure 15; the latter shows the carbon-solution contact angle as function of time, with water, DDBS 0.5mM or EGPE 2.0mM solutions and a mixed solution containing DDBS(0.5mM)-EGPE(2.0mM). The results show that the high contact angle observed with water (typical of non-wetting behaviour of hydrophobic particles) is only marginally reduced with either the EGPE or the DDBS solutions at the selected dosage.

On the other hand, the DDBS-EGPE mixture greatly reduces the carbon-solution contact angle, i.e., improves wetting. It is important to note, however, that the surface tension of the DDBS and mixed DDBS-EGPE solutions are only slightly different, i.e., 40 vs. 36 mN.m⁻¹. To achieve a similar wetting contact angle with DDBS alone, the concentration had to be increased to 2.0mM, and the solution surface tension was 29mN.m⁻¹. Consequently, the enhanced wetting observed in the presence of EGPE is not only a consequence of a reduced surface tension. Similar observations have been reported for n-alcohol adsorption on hydrophobic particles²³. The synergistic wetting effects induced by EGPE and DDBS for activated carbon as described above were also observed with the other solids, although to varying extents.

Qualitative Mechanism Operating in Chemical Mitigation of FA-Carbon Effects on Air Entrainment

Based upon the observations collected in this and earlier investigations, the influence of FA-carbon on air entrainment and the mitigation of these effects by chemical additives can be rationalized from the schematic diagrams in Figure 16, showing (A) a surfactant film at an air-solution or air/cement paste interface. The film cohesion and integrity is ensured by attractive forces between the hydrocarbon chains of the surfactant

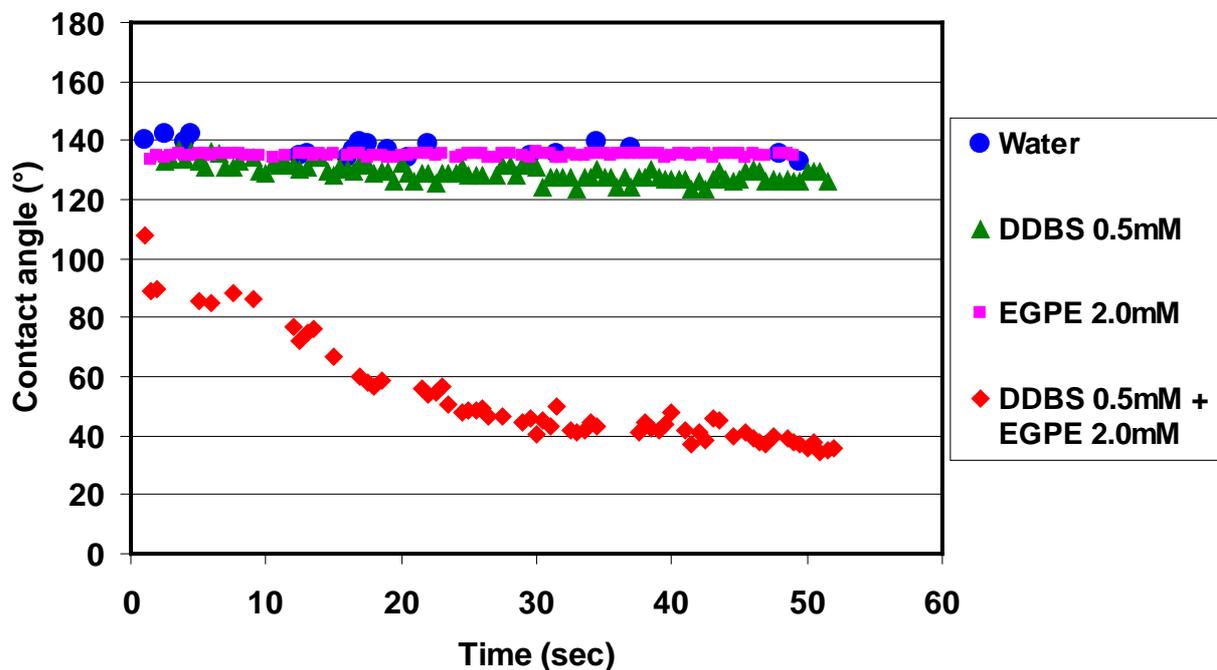


Figure 15: Contact angle at carbon/liquid interface with activated carbon.

molecules, balanced by electrostatic repulsive forces between the ionic head groups (at the paste/air interface, other colloidal phenomena can also contribute to film stability as discussed earlier⁸.

As shown in (B), hydrophobic particles can disrupt the surfactant film by adsorbing part of the surfactant molecules, the mechanism generally invoked to explain the concrete air entrainment depression due to FA-carbon. On the other hand, regardless of their adsorbing capacity, fine hydrophobic particles (particles with low surface energy) can insert themselves into the hydrocarbon portion of the film, leading to film rupture^{11,18-21,23}. Carbon particles contained in FA most likely induce concrete air depression through both mechanisms, in varying proportion depending on the type of carbon, particle size, surface area and porosity.

Hydrophilic particles (particles with high surface energy) may also adsorb surfactant molecules (though likely less so than similar size hydrophobic particles); in addition, they can interact with the hydrophilic portion of the surfactant film, possibly providing a film stabilization effect²⁴.

When a hydrophobic carbon particle adsorbs EGPE molecules (in the presence of the surfactant), its hydrophilic character is increased, as evidenced by enhanced wetting; this is illustrated in Figure 16 (C). This surface modification of the carbon particle will result in reduced interaction with the hydrocarbon portion of the film (weaker disruptive effects) and increased interactions with the hydrophilic surface of the film (potential stabilization effects). Hence, although the adsorbed EGPE may not greatly reduce

surfactant adsorption, it still plays a major role in preventing the deleterious effect of carbon particles on air entrainment. In this framework, it is readily understood why the sacrificial agent EGPE is neutral with respect to air entrainment: once sufficient EGPE is adsorbed to change the surface properties of the particle, further addition will have no influence, i.e., EGPE not being itself an air-entraining agent.

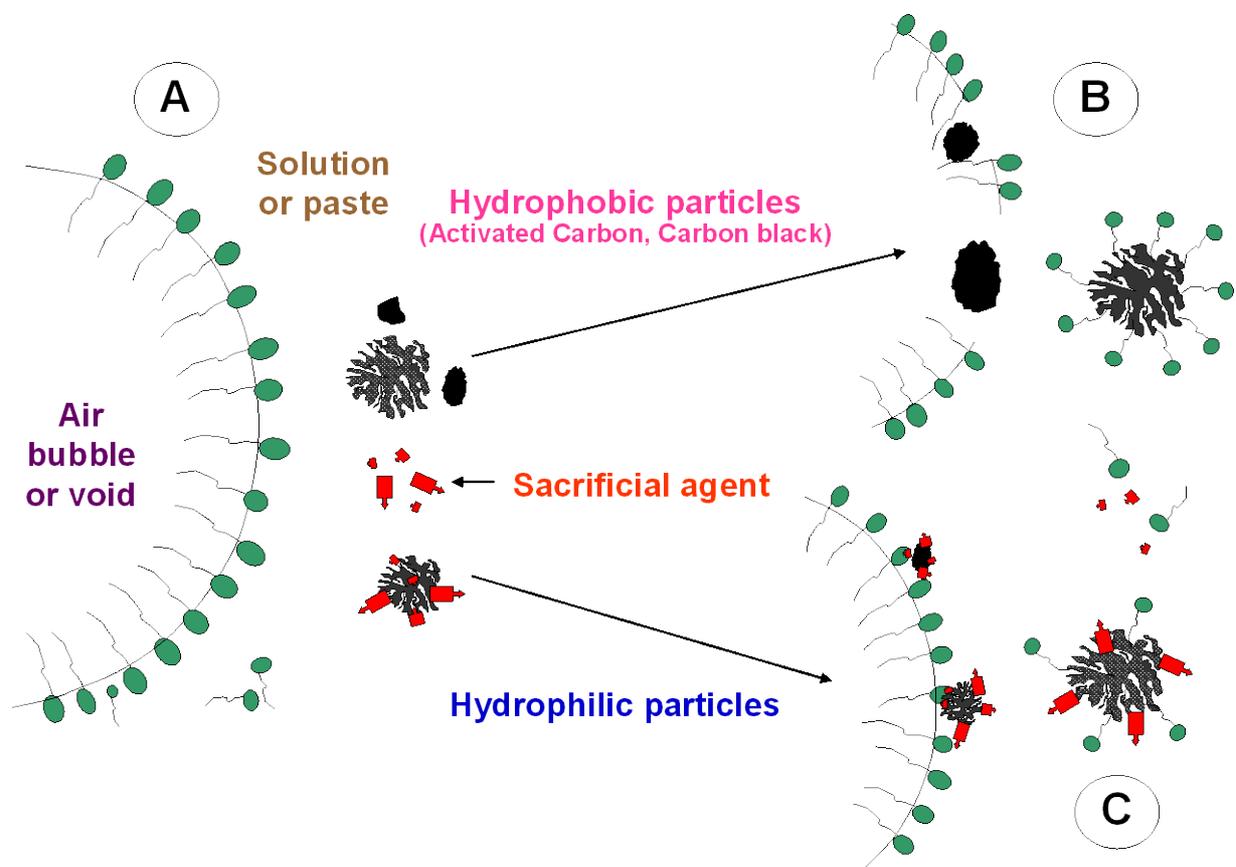


Figure 16: Schematic representation of different phenomena occurring at the surfactant film interface. A: initial state of film; B: effect of hydrophobic particles leading to film rupture; C: protective influences of sacrificial agent.

CONCLUSION

The combined experimental results derived from studies on air entrainment in cement pastes, surfactant foam generation and particle/solution interfacial phenomena (adsorption, wetting) provide a fairly comprehensive description of how carbon particles remaining in fly ash can impede concrete air entrainment. In the mechanistic model proposed, disruption of the surfactant film at the paste/air interface of a concrete air void, as well as at the solution/air interface of an air bubble, are caused by two concomitant effects: 1- surfactant adsorption by the carbon particle and 2- interaction of the hydrophobic particle directly in the hydrocarbon region of the surfactant film.

Complementary investigations including admixtures which can mitigate the FA-carbon effect, i.e., 'sacrificial admixtures', also offer an explanation for the mode of action of these admixtures. The latter prevent the deleterious carbon effect on air entrainment by altering the surfactant adsorption and the surface energy (wetting behaviour) of the carbon particles. The relative importance of contributions from these two effects will depend on the type of carbon and the physico-chemical properties of the particles; however, the results currently available point to the prominence of surface energy modifications by the sacrificial admixture. The proposed mechanism also explains the observation (and requirement) that the addition of excessive dosages of the sacrificial agent has no detrimental consequences on air entrainment.

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