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Investigating Techniques for Evaluating Fly Ash Behaviour in Air-entrained Concrete

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Abstract

The paper describes research from a study carried out to investigate techniques for evaluating fly ash influences on air-entrainment in concrete and covers the potential of dye adsorption tests, i.e. using methylene blue (MB) and acid blue 80 (AB80), in this role. The MB test is essentially that given in BS EN 933-9 (normally used for the assessment of fines in sand) and involves visual determination of an endpoint, while the AB80 test (similar to those used for examining activated carbon) is spectroscopic and, therefore, instrument-based. Following the determination of suitable procedures for the tests, their evaluation with fly ashes covering a range of properties is described through comparisons against parameters including, loss-on-ignition and specific surface area (measured by N_2 adsorption). Relationships are presented that examine the dye adsorption of fly ash with respect to the air-entraining admixture demand to achieve a target air content range (5.0 ± 1.0%) in corresponding concretes. These indicate strong correlations for the materials used. Consideration is given to how the dye adsorption tests could be applied in air-entrained fly ash concrete production.

Keywords: fly ash, air-entrainment, dye adsorption tests, loss-on-ignition, specific surface area, admixture demand, concrete.

1 Introduction

Air-entrainment in concrete is a well-established means of improving resistance to freeze/thaw damage, by providing small air bubbles, distributed through the material. The unburnt carbon present in fly ash can affect the process of entraining air and ideally variations in the quantity of this component should be minimised to assist concrete production [1]. Identifying how particular material combinations (fly ash/air-entraining admixture (AEA)) will behave is, therefore, an important factor with regard to their use in concrete.

Various techniques to evaluate this have been considered in the literature [2-6]. Of these, the foam index is perhaps the most widely known and adopted. Indeed, research has been carried out recently towards standardizing aspects of the procedure, e.g. material quantities, types of test vial and shaking [7, 8], however, it can still be influenced by the operator (i.e. determination of the endpoint). An alternative to this may be dye adsorption tests. These have been applied for characterising activated carbons [9-11] and in the assessment of fly ash adsorption capacity for wastewater treatment [12]. A test for fly ash, with methylene blue (MB) dye, is also described in a Japanese standard [13].

This type of approach essentially involves (i) the incremental addition of dye to a fly ash / de-ionised water slurry, or (ii) exposure of the material to a dye solution, until equilibrium is achieved. In both cases, determining how much dye has been adsorbed when this condition is reached is an integral part. This paper considers research carried out to investigate the potential of dye adsorption tests, (and builds on that described earlier [8, 14]) to assist in determining fly ash/AEA behaviour for use in concrete.

2 Summary of Fly Ash/AEA Behaviour and its Evaluation

The effect of fly ash on the dose of AEA required to achieve target air contents in concrete has received wide coverage in the literature. Research has established the role of unburnt carbon on AEA demand and that these type of admixtures are adsorbed by this in fly ash. Such effects tend to influence the stability of the air-water/cement interface and thereby reduce the level of air entrained [15, 16]. As a result, AEAs specially formulated for use with fly ash are now available [1, 8].

The behaviour of fly ash with AEA has been reported to depend on a number of factors including, (i) carbon content; (ii) carbon type (e.g. coarse particles or soot); (iii) specific surface area of fly ash (porosity); (iv) accessibility of AEA to particle surfaces (internal and external); and (v) the chemical nature of these surfaces (polarity) [2, 7, 16-20].

The active sites, responsible for AEA adsorption, are mainly found on the carbon surface [16]. The surface area of this component in fly ash can be much greater than its mineral part [19]. Thus, although it may be present at low levels in the material, carbon (depending on its porosity) can contribute significantly to the surface area and to variations noted for this between different fly ashes.

Testing the loss-on-ignition (LOI) can provide an approximate measure of the level of carbon in fly ash. However, while this is often used to characterise the material, several studies have found that it has limitations as an indicator of fly ash/AEA behaviour in concrete [17-19]. Given the various factors described, other approaches, as noted above [2-8], have been considered towards evaluating this aspect of fly ash.

3 Range of Fly Ashes Used in the Study

Fly ashes were obtained from six UK sources for the study. These were low-lime and covered various effects including sampling at different times of year, high and low fineness/LOI and co-combustion, and therefore provided fly ash with a range of properties. Details of these materials have been given previously [8, 14], and they are summarized in Table 1.

4 Methylene Blue Tests

4.1 Test procedure

Methylene blue is a dye, used in various material tests, e.g. determination of the surface area and cation exchange capacity of clay minerals [21], evaluation of activated carbon [10] and for the assessment of fines in sand for use in concrete. The latter is described in the European standard BS EN 933-9 [22] and this procedure was generally adopted to investigate fly ash in the study. The reagent used was methylene blue trihydrate (molecular formula, $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, with molecular weight 373.9 g).

The test carried out is similar in principle to the foam index method [8, 23]. A 200 g fly ash sample was introduced to 500 ml of de-ionised water and then the slurry mixed continuously using a propeller-type stirrer, see Fig. 1(a). After 5 minutes, 5 ml of known concentration (10.0 g/l is recommended in the standard) of MB dye was added to the slurry and with continued mixing a stain test carried out on filter paper after 1 and 5 minutes. Formation of successive halos, during the stain test, at these specified periods indicates the endpoint of the test, see Fig. 1(b). The MB value of the sample was calculated from the total uptake of dye per unit mass of fly ash to reach the endpoint.

4.2 Evaluation

The relationships between MB value, specific surface area (measured by N_2 adsorption) and LOI are shown in Fig. 2. A strong correlation between MB value and specific surface area was obtained. However, as found earlier with the foam index test [8], this did not correlate as well with the LOI of the fly ashes.

The concentration of MB dye (10.0 g/l) specified in BS EN 933-9 [22], seemed to be high for determining relative differences in adsorption between fly ashes, especially those of low LOI. Therefore, a set of 5 fly ashes were tested using a 5.0 g/l dye solution, i.e. halving the increment concentration added.

As indicated in Fig. 3, an improvement in correlations between the MB value, specific surface area and LOI was found with the lower concentration dye. In addition, with the 5.0 g/l solution, a lower MB value was obtained in most cases, see Fig. 4, which suggests that better precision may be obtained with the test at this concentration. Another factor that could influence the results with the test is operator judgement, with regard to identifying the endpoint. However, this should have a small effect, as detection of halos is reasonably straightforward.

5 Acid Blue 80 Tests

5.1 Test procedure

The acid blue 80 (AB80) test is based on that described previously [9-11] and involves spectrophotometric measurements of the chemical reagent's absorbance. A laboratory standard AB80 dye (molecular formula $C_{32}H_{28}N_2Na_2O_8S_2$, molecular weight 678.7g, and peak absorbance wavelengths 282, 581 and 626 nm) was used, since there is experience of testing this dye with activated carbon and it has similarities to components used in AEAs [11, 24]. The test involved exposing a quantity of fly ash to a defined AB80 solution concentration / volume for a given time period, filtration and determination of the remaining AB80 in solution, see Fig. 5(a). The quantity of dye taken up per unit mass of fly ash was the AB80 adsorption. A test procedure for fly ash has been described previously [14] and hence only brief coverage is given here.

The equipment used for the tests was a digital colorimeter (*Fisher Scientific, Colorimeter model 45*) with an absorbance measurement range from 0.00 – 1.99, a resolution of 0.01 and fixed wavelength filters, see Fig. 5(b). Initial experiments established relationships (calibrations) between AB80 concentration and absorbance for the filters considered (630 and 580 nm, with tests mainly using the former). Corrections for dye losses, in filter paper, during filtration were also quantified. Tests were then made to determine suitable operating conditions with fly ash. As indicated in Fig. 6(a), for example, a target remaining AB80 concentration was appropriate for measurements with the equipment

(630 nm filter, 10 – 85 mg/l), and hence small adjustments to the sample size for low/high LOI fly ash were used in some cases to achieve this. Similarly, while differences in adsorption between the lowest and highest LOI fly ashes were identifiable at 10 minutes, up to 30 minutes was required to obtain equilibrium for the latter material, see Fig. 6(b) (the tests described here were carried out for 60 minutes). A summary of the main parameters / relationships established for the tests with fly ash is shown in Table 2.

5.2 Evaluation

The relationship between AB80 adsorption, specific surface area and LOI of fly ash is given in Fig. 7. This indicates that there was a general correlation between AB80 adsorption and LOI, however, this was stronger with specific surface area. Further analysis of the data gave a strong correlation between the two dye adsorption tests, suggesting that similar effects were occurring between these and fly ash, see Fig. 8. The levels of uptake between the two dyes indicate that approximately twice as much AB80 was adsorbed by fly ash, which may relate to their different properties and test arrangements used.

As noted above, the literature indicates that LOI may have limitations as a measure of how fly ash influences air-entrainment in concrete. In contrast, specific surface area is considered to provide a good indication of this [20]. For both of the dye tests, the relationships noted suggest that these have potential for evaluating fly ash/AEA behaviour.

In order to further investigate this, the research progressed to consider how these properties relate to entrainment of air in fly ash concrete.

6 Air-Entrained Concrete Studies

Details of the materials and concretes used, and their preparation have been reported previously [8, 14] and they are, therefore, briefly summarised here.

6.1 Materials used

An AEA, suitable for use with fly ash in practice (AEA C1) and a standard chemical (surfactant, sodium dodecyl benzene sulfonate (SBDS), AEA S) were considered for air-entrainment in the concretes. The concentration of the latter for the tests was set at 0.01 M.

A 52.5 N strength class Portland cement (PC), see Table 1, with gravel aggregates (maximum size 20 mm) and a medium grade sand were used in the concretes. The constituent materials all met the requirements of the relevant European standards (where applicable).

6.2 Concretes, mixing and test procedure

During these tests, the AEA doses required to entrain 5.0 ± 1.0% air in reference PC and fly ash (using 6 of the materials referred to above; at a level of 30%) concretes were evaluated.

The free water and cement contents of these were 175 and 350 kg/m^3 respectively, with a sand/total aggregate ratio of 0.42. The estimated plastic densities of the air-entrained PC and fly ash concretes were 2265 and 2225 kg/m^3, respectively.

While AEA C1 was introduced to concrete, as-supplied, higher doses were required for AEA S (due to its low concentration, 0.01 M). Thus, AEA S was used by replacing water with this in the mix. Concrete was prepared with a 0.035 m^3 horizontal pan mixer, using a similar method to that of BS 1881-125 [25].

Trial mixing was carried out with the AEAs to determine the doses required to achieve the target air content range and measurements of this property on fresh concrete were made to BS EN 12350-7 (pressure method) [26].

6.3 AEA dose evaluation with MB and AB80 adsorption tests

The admixture doses corresponding to the target air content range are shown in Fig. 9. The general ranking between fly ashes for the two admixtures was similar, although the quantities needed were different. It is also apparent from the data that the doses varied for fly ash concretes by between approximately 1 and 7 times the quantity used in the references, and that these also followed the specific surface area of the material.

The relationships between AEA dose required to achieve the target air content in fly ash concrete (with respect to those of the reference PCs) and dye adsorption (MB value and AB80 adsorption) are given in Fig. 10. The data indicate that the admixture dose increased both with MB value and AB80 adsorption, and that strong correlations were obtained between these for both AEA C1 and AEA S.

While back extrapolation of the data in Fig. 10 for the MB test passed through the abscissa, that for AB80 adsorption crossed the ordinate at a value of about 1.0 (i.e. similar to the reference PC concrete admixture dose, with no fly ash). This may reflect the different procedures involved between the two dye tests, i.e. incremental additions, or exposure to the dye solution; and observations of the endpoint and instrumental measurements. Furthermore, the AB80 test results enabled the active and adsorbed parts of the AEAs to be identified [14].

Overall the data suggest that the methods could be used to estimate AEA dose requirements for fly ash concrete.

7 Concluding Remarks

The use of dye adsorption techniques from other fields to quantify the effect of fly ash on air-entrained concrete is described. Following initial considerations, e.g. calibrations, refinements to these tests to enable adoption with fly ash are considered, and suitable test conditions established. These covered factors such as dye concentration, sample size and contact time.

It is shown that the adsorption properties of fly ash gave general agreement with LOI, but stronger correlations were obtained with specific surface area, the latter of which is considered in the literature to provide a good indication of fly ash/AEA behaviour.

Between the two dye tests, the AB80 adsorption method perhaps offers advantages given that it is instrumental, thereby eliminating operator influence. However, the various relationships obtained with the MB tests were comparable to this, but without the need for a special instrument to carry them out.

As suggested for the foam index test [8], with further work, these methods could be adopted as evaluation-type tests for fly ash with regard to its use in this application. In addition, they could be used to assist in the production of air-entrained fly ash concrete. For example, based on the results given in Fig. 10 (b), Table 3 shows the variations in admixture demand to entrain 5.0 ± 1.0% air in concrete for the materials used in the study, with respect to changing fly ash properties, given in terms of AB80 adsorption.

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References

[1] Concrete Society (2011). Cementitious materials: the effect of GGBS, fly ash, silica fume and limestone fines on the properties of concrete. Technical Report 74. *The Concrete Society*, Camberley, Surrey, UK.

[2] Gao Y M, Shim H S, Hurt R H and Suuberg E M (1997). Effects of carbon on air entrainment in fly ash concrete: The role of soot and carbon black. *Energy & Fuels,* Vol. 11**,** No. 2, pp. 457-462

[3] Yu J, Külaots J, Sabanegh N, Gao Y, Hurt R, Suuberg E and Mehta A (2000). Adsorptive and optical properties of fly ash from coal and petroleum coke co-firing. *Energy and Fuels*, Vol. 14, No. 3, pp. 591-596.

[4] Baltrus J P and LaCount R B (2001). Measurement of adsorption of air-entraining admixtures on fly ash in concrete and cement. *Cement and Concrete Research*, Vol. 31, No. 5, pp. 819-824.

[5] Pedersen K H, Andersen S I, Jensen A D and Dam-Johansen K (2007). Replacement of the foam index test with surface tension measurements. *Cement and Concrete Research*, Vol. 37, No. 6, pp. 996-1004.

[6] Stencel J M, Song H and Cangialosi F (2009). Automated foam index test: Quantifying air entraining agent addition and interactions with fly ash–cement admixtures, *Cement and Concrete Research,* Vol. 39, No. 4, pp. 362-370.

[7] Folliard K, Hover K, Harris N, Ley M T and Naranjo A (2009). Effects of Texas fly ash on air-entrainment in concrete: Comprehensive report*. Center for Transportation Research, The University of Texas at Austin*, Austin, TX, USA, 577 p.

[8] McCarthy M J, Islam G M Sadiqul, Csetenyi L J and Jones M R (2012). Refining the foam index test for use with air-entrained fly ash concrete. *Magazine of Concrete Research*, In Press.

[9] ASTM D3860 (2008). Standard practice for determination of adsorptive capacity of activated carbon by aqueous phase isotherm technique. *ASTM International*, West Conshohocken, PA, USA.

[10] Hameed B H, Din A T M and Ahmad A L (2007). Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *Journal of Hazardous Materials,* Vol. 141**,** No. 3, pp. 819-825.

[11] Zhang Y and Nelson S (2007). Development of a new method to replace the foam index test. *World of Coal Ash (WOCA)*, 7-10 May 2007, Covington, KY, USA.

[12] Wang S, Boyjoo Y and Choueib A (2005). A comparative study of dye removal using fly ash treated by different methods. *Chemosphere*, Vol. 60, No. 10, pp. 1401-1407.

[13] JCAS I-61 (2008). Measurement of the amount of methylene blue absorption by fly ash. Test manual—IV, *Japan Cement Association*, Japan, pp. 42–45 (In Japanese).

[14] McCarthy M J, Islam G M Sadiqul, Csetenyi L J and Jones M R (2012). Colorimetric evaluation of admixture adsorption by fly ash for use in air-entrained concrete. *Materials and Structures*, In Press.

[15] Hachmann L, Burnett A, Gao Y M, Hurt R H and Suuberg E M (1998). Surfactant adsorptivity of solid products from pulverized-coal combustion under controlled conditions. *Twenty-Seventh Symposium (International) on Combustion,* Vols. 1 and 2, pp. 2965-2971.

[16] Pedersen K H, Jensen A D, Skjøth-Rasmussen M S and Dam-Johansen K (2008). A review of the interference of carbon containing fly ash with air entrainment in concrete. *Progress in Energy and Combustion Science,* Vol. 34**,** No. 2, pp. 135-154.

[17] Hill R L, Sarkar S L, Rathbone R F and Hower J C (1997). An examination of fly ash carbon and its interactions with air entraining agent. *Cement and Concrete Research,* Vol. 27**,** No. 2, pp. 193-204.

[18] Maroto-Valer M M, Taulbee D N and Hower J C (2001). Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation. *Fuel,* Vol. 80**,** No. 6, pp. 795-800.

[19] Külaots I, Hurt R H and Suuberg E M (2004). Size distribution of unburned carbon in coal fly ash and its implications. *Fuel,* Vol. 83**,** No. 2, pp. 223-230.

[20] Spörel F, Uebachs S and Brameshuber W (2009). Investigations on the influence of fly ash on the formation and stability of artificially entrained air voids in concrete. *Materials and Structures,* Vol. 42**,** No. 2, pp. 227-240.

[21] Hang P T and Brindley G W (1970). Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (Clay-organic studies XVIII). *Clays and Clay Minerals*, Vol. 18, No. 4, pp. 203-212.

[22] BS EN 933-9 (1999). Tests for geometrical properties of aggregates: Assessment of fines – Methylene blue test. *BSI*, London, UK.

[23] Dodson V H (1990). Concrete Admixtures, *Van Nostrand Reinhold*, New York, NY, USA, ISBN: 0-442-00149-5, 211 p.

[24] Environment Canada (2008). Screening assessment for the challenge — Benzene-sulfonic acid, 3,3' [(9,10-dihydro-9,10-dioxo-1,4-anthracenediyl) diimino]bis [2,4,6-trimethyl] disodium salt (Acid Blue 80, CAS RN 4474-24-2). Ottawa, Canada, 27 p.

[25] BS 1881-125 (1986). Testing concrete: Methods for mixing and sampling fresh concrete in the laboratory, *BSI*, London, UK.

[26] BS EN 12350-7 (2009). Testing fresh concrete: Air content – Pressure methods. *BSI*, London, UK.

Table 1. Characteristics of fly ashes and PC used [8]

Characteristic	Fly ash										PC
	A-S Jan	A-N Jul	B-S Jul	C-S Jan	C LLHF	D STI	E UF	E EN1	E EN2	F CC	
Key physical properties											
LOI [a], %	3.8	5.1	5.0	4.3	3.1	2.6	3.0	3.9	6.4	7.6	-
Spec. surface area, m²/g	1.55	2.64	2.21	1.88	2.10	1.12	2.46	3.60	5.20	5.02	1.60[b]
45 μm sieve residue, %	9.6	19.3	11.2	9.9	29.1	21.8	4.8	20.4	23.4	28.8	-
Main oxide composition, %											
CaO	3.7	4.3	2.6	2.7	2.0	2.6	4.9	5.2	6.6	4.0	65.0
SiO_2	50.8	48.1	47.5	48.8	46.5	53.5	56.2	52.2	53.8	45.8	21.0
Al_2O_3	21.1	22.9	20.2	23.0	21.4	24.0	19.2	18.8	21.4	25.2	5.3
Fe_2O_3	8.7	7.1	9.1	8.0	10.4	4.4	5.0	5.1	5.2	7.4	2.8
MgO	1.9	1.7	1.5	1.5	1.3	0.9	1.5	1.5	1.4	1.5	1.0
K_2O	2.8	2.3	3.0	2.8	3.3	2.3	1.9	2.1	1.4	2.2	0.6
Na_2O	1.6	1.5	0.9	1.2	1.7	0.8	0.9	1.1	1.2	0.7	0.3
SO_3	1.0	1.3	1.2	0.7	0.9	0.3	0.5	0.6	0.6	0.9	3.0
Mineral composition, %											
Quartz	14.1	9.7	12.6	9.4	6.7	4.3	16.2	19.4	11.1	6.3	-
Mullite	9.7	16.0	14.0	13.2	5.7	12.5	13.0	18.6	11.6	17.1	-
Haematite	2.8	2.7	3.6	2.4	3.4	-	1.5	0.9	1.4	2.0	-
Magnetite	0.2	0.4	0.2	0.3	-	0.1	0.1	0.1	0.2	0.2	-
Amorphous / others	73.2	71.3	69.7	74.7	84.2	83.1	69.2	61.0	75.7	74.3	-

[a] *LOI carried out at 975°C. Initial moisture content of fly ashes <0.5%.*

[b] *Blaine fineness of PC, 550 m^2/kg.*

- Not detected / tested.

Table 2. Summary of main parameters / relationships established for AB80 adsorption tests

Aspect of the test	Details
Concentration of AB80 solution, mg/l	100
Fly ash sample size, g	2.0
Quantity of AB80 solution per test, ml	100
Contact time, minutes	30 [a]
Calibration equation [b]	$y_1 = 43.32x_1 – 1.06$
Equation for filter paper correction [c]	$y_2 = 1.06x_2 + 0.21$

[a] *In the tests reported, a contact time of 60 minutes was used.*

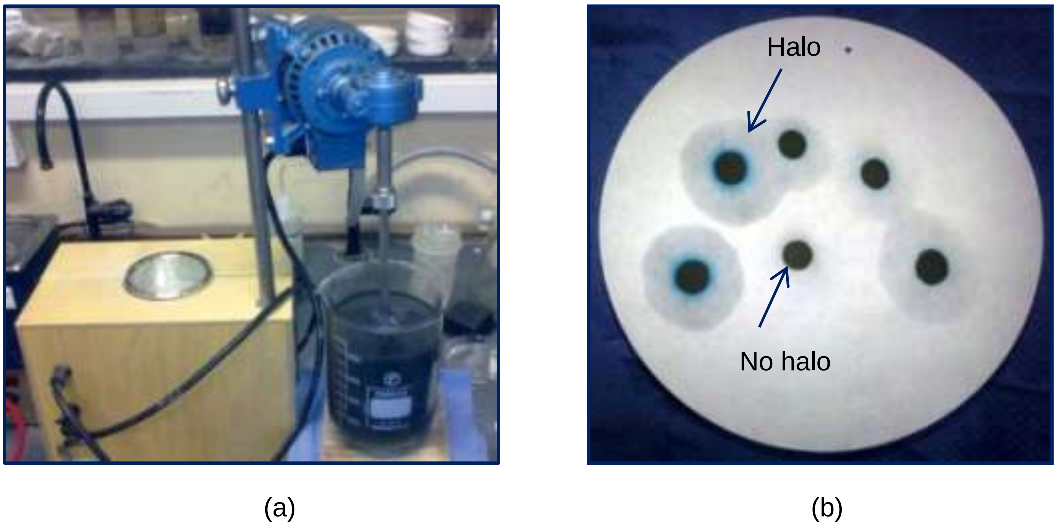
[b] y_1 = *AB80 concentration in solution, mg/l; and* x_1 = *absorbance (with 630 nm filter).*

[c] y_2 = *AB80 concentration before filtration, mg/l; and* x_2 = *AB80 concentration after filtration, mg/l.*

Table 3. AB80 adsorption and AEA demand to entrain 5.0 ± 1.0% air in concrete

AB80 adsorption, mg/g fly ash	AEA C1, ml/kg PC+fly ash	AEA S, ml/kg PC+fly ash
0	0.8	21.3
1	1.8	46.2
2	2.9	71.1
3	4.0	95.9
4	5.1	120.8

Fig. 1 (a) MB test set up and (b) blue halo around fly ash on filter paper indicating the test endpoint



(a) (b)

Fig. 2 Relationship between MB value (with 10 g/l solution), fly ash specific surface area and LOI

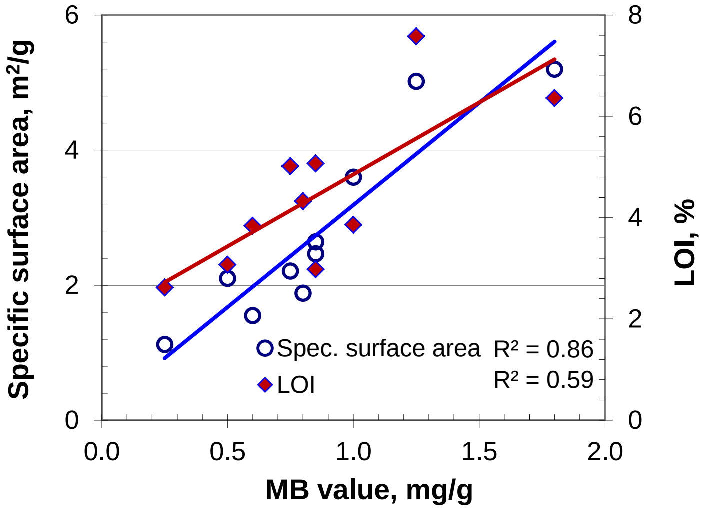


Fig.3 Relationship between MB value (with 5 g/l solution), fly ash specific surface area and LOI

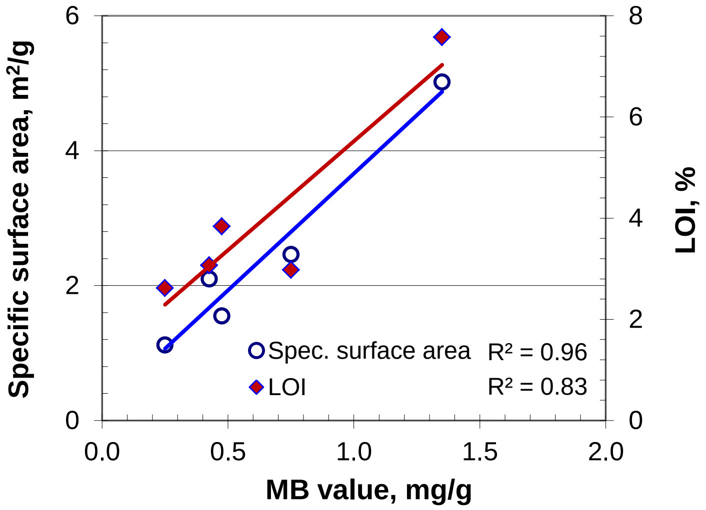


Fig.4 Comparison between MB values using different dye concentrations

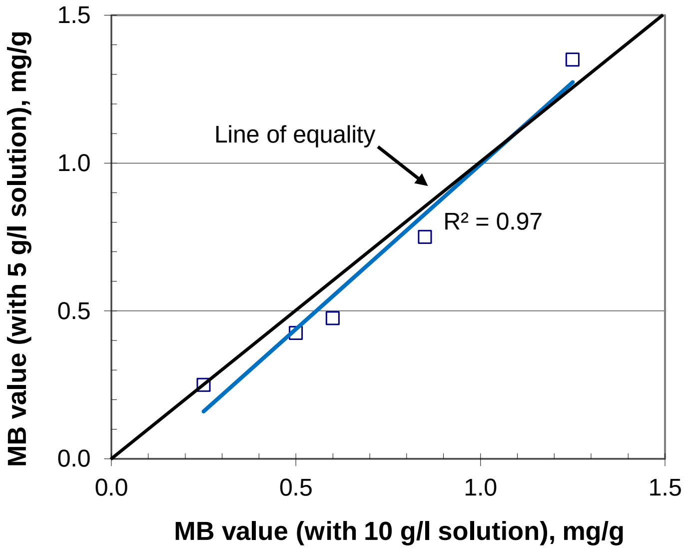


Fig. 5 (a) exposing fly ash to AB80 solution and (b) concentration determination with colorimeter

(a)

(b)

Fig. 6 Effect of (a) fly ash sample size and (b) contact time on AB80 measurements

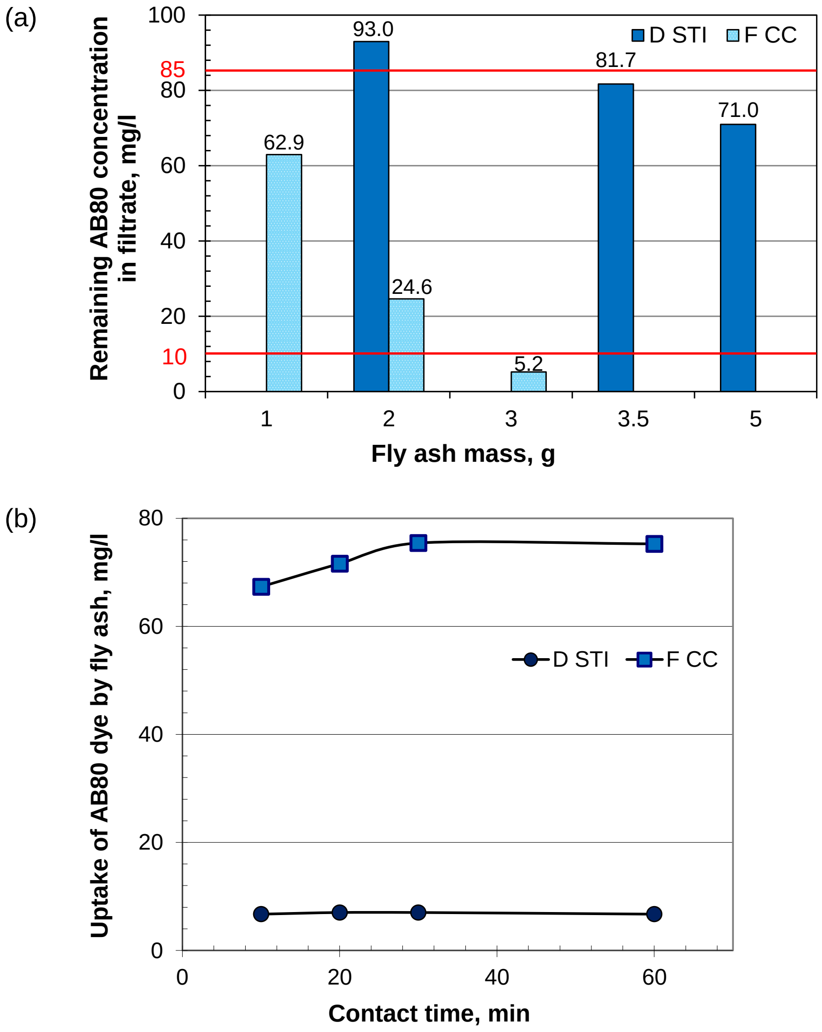


Fig. 7 Relationship between AB80 adsorption, fly ash specific surface area and LOI

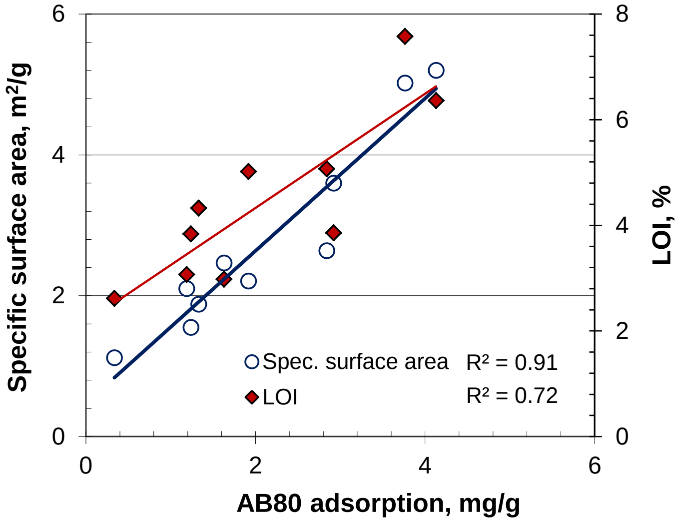


Fig. 8 Relationship between AB80 adsorption and MB value

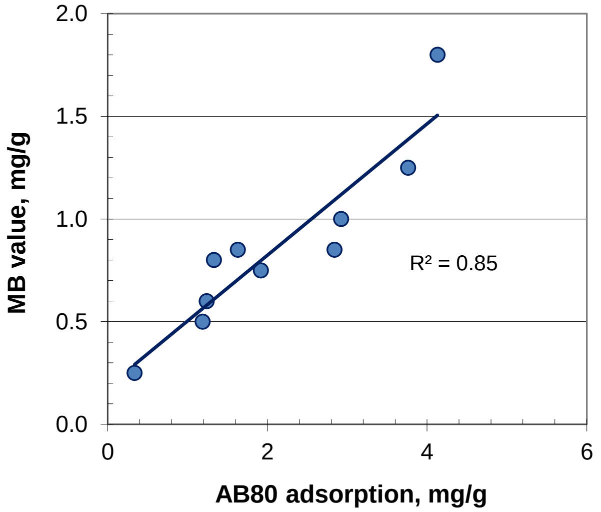


Fig. 9 Doses for achieving a target air content (5.0 ± 1.0%) in concrete with AEA C1 and AEA S

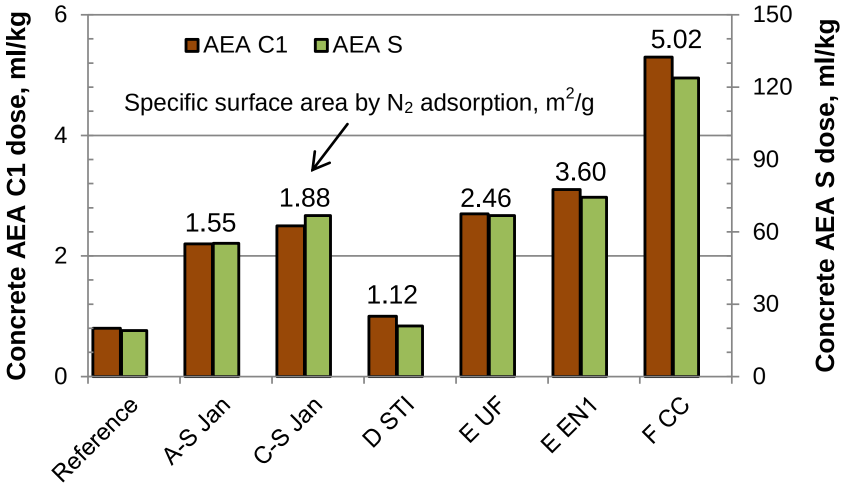


Fig. 10 Relationships between (a) MB value and (b) AB80 adsorption and AEA dose for achieving a target air content (5.0 ± 1.0%) in concrete with AEA C1 and AEA S