Investigation of Alkali-Silica Reaction in Concretes with Biomass Fly Ash

¹Rajamma R.^{1*}

¹University of Aveiro, Department of Civil Engineering/CICECO, 3810-193 Aveiro, Portugal.

Soares D.²

² National Laboratory for Civil Engineering (LNEC), Materials Department, 1700-066 Lisbon, Portugal. Esteves T.C.³, Silva A.S.², Labrincha J.A.³, Ferreira V.M.¹,.

³University of Aveiro, Department of Ceramics and Glass Engineering/CICECO, 3810-193 Aveiro, Portugal.

Abstract

The alkali–silica reaction (ASR) in concrete occurs by reaction of certain silica phases in the aggregates with alkalis and hydroxide ions in the pore solution of the hydrating cement to produce a hydrous alkali-silicate gel. This gel can swell by incorporating large amounts of water, causing severe and irreversible expansion and cracking of the concrete. The level of expansion and disruption in concrete containing reactive aggregate depends on the alkali content of the concrete and the reactivity of the aggregate. The levels of alkali that trigger the expansion depend, however, on the reactivity of the aggregates. Alkalis from Portland cement (OPC) are one of the major sources of these ions in concrete. The use of industrial by-products such as fly ash and slag has been found to be an effective preventive measure against ASR in concrete.

This article presents the performance of biomass fly ash - an industrial by-product - in the mitigation/inhibition of ASR in concrete. Laboratory expansion tests were conducted to evaluate the performance of biomass fly ash, in replacement of OPC by 20% and 30% (w/w) in the experiments (ASTM C1260/ASTM C1567). The results revealed that biomass fly ash has a good potential in the expansion inhibition due to ASR.

Originality

In recent years, pressures on global environment and energy security have led to an increasing demand on renewable energy sources, and diversification of Europe's energy supply. Among these resources the biomass could exert an important role, since it is considered a renewable and CO_2 neutral energy resource once the consumption rate is lower than the growth rate, and can potentially provide energy for heat, power and transports from the same installation. Currently, most of the biomass ash produced in industrial plants is either disposed of in landfill or recycled on agricultural fields or forest, and most times this goes on without any form of control. However, considering that the disposal cost of biomass ashes are raising, and that biomass ash volumes are increasing worldwide, a sustainable ash management has to be established. It is reported that the biomass fly ash collected as wastes from the industrial plants in Portugal can be effectively used as a cement substitute. The present work aims to discuss the role of biomass fly ash on the ASR mechanism in concrete.

Chief contributions

The biomass fly ash was collected from an industrial plant in Portugal and was sieved through 75 micron mesh and washed prior to the incorporation in mortars and concretes. The characterisation of the ash was done using different techniques such as particle size distribution, loss on ignition, TGA/DTA, XRD, XRF and pozzolanic activity test. The biomass fly ash is irregular in shape and fine in nature. The chemical characterisation revealed that the biomass fly ash is similar to a class C fly ash and contain around 25% CaO, being expected to react also hydraulically.

Accelerated mortar-bar tests were conducted according ASTM C 1260/ASTM C 1567 to evaluate the behavior of the biomass fly ash in the ASR inhibition mechanism. These mortars were done with 20 and 30% of cement substitution, in weight, by fly ash. The results obtained shown a clear reduction in expansion due to ASR in the biomass fly ash mortars. Currently, we are doing the concrete prism expansion tests according the RILEM AAR-3 and RILEM AAR-4 test methods to confirm the good response of biomass fly ash in mortar-bar tests.

Keywords: Alkali-silica reactions; Biomass fly ash; Concretes; Industrial by-products.

¹ Corresponding author: E-mail <u>rejini@ua.pt</u>, Tel +351 934118726

Introduction

Damage of concrete structures by the alkali silica reaction (ASR) has become a major concern in construction. The mechanisms behind the ASR formation are still not completely understood. Anyway it is widely accepted that ASR gel product is formed by the reactions between alkali cations (K^+, Na^+) and hydroxyl groups (OH^-) present in the pore solution and poorly crystallized siliceous minerals found in some aggregates [Lane, 1999]. Swelling of this gel in the presence of excess moisture results in the expansion and cracking of the concrete. The use of industrial wastes, such as fly ash or blast-furnace slag have been proved effective means of controlling the deleterious expansions due to ASR [Malvar, 2006, Haster et al., 2005]. Researches have proved the significant possibility of using biomass fly ash, another industrial waste material for cement replacement [Dockter, 2003, Wang, 2007, Rajamma et al, 2009]. However, biomass fly ash is excluded from additions in concrete according to the current standards because of its non-coal origin. Recently, the new standard EN-450-1 included fly ash obtained from co-combustion of specific co-combustion biomass materials up to 20% by mass of the total fuel. Class C fly ashes with high CaO content are also reported to be useful in mitigating ASR and biomass fly ashes usually are high calcium fly ashes. [Maciejewska et al., 2006, Dockter, 2009]. However, the high alkali content in biomass ash seem to be a big concern of ASR in concrete and detailed investigation is needed on the role of biomass fly ash in the ASR expansion of concretes.

The present work aims to discuss the role of biomass fly ash on the ASR mitigation mechanism using the ASTM C1260/ASTM C1567 procedure of accelerated mortar-bar tests. The biomass fly ashes used in the investigation are collected from two industrial power plants located in Portugal which are reported similar to a class C type fly ash in chemical composition.

Experimental procedure

Biomass fly ash characterization

The biomass fly ash samples used were collected from the electrostatic precipitators of a biomass thermal power plant and of a co-generation plant, both located in Portugal. Both plants use forest wastes as main fuel (mainly eucalyptus wastes, resulting from logging and wood processing activities). The fly ash F1 was collected from a biomass thermal power plant dedicated to electricity production, which uses forest residues for energy production and water cooled grate furnace for fuel combustion. The fly ash F2 was collected from a biomass co-generation plant, from a pulp and paper industry in which fluidised bed technology is used for the firing process.

The fly ashes were sieved through a 75 µm mesh and underwent a leaching process with distilled water prior to incorporation in the mortars specimens in order to control the soluble salts content in the fly ashes. The particle size distributions of the fly ashes were studied using a Coulter LS particle size analyser (LS230FM). The surface area of the fly ashes was determined by BET (Brunauer, Emmett, and Teller method). The mineral compositions were characterised by X-ray diffraction (XRD) (RIGAKU-Geigerflex, power 40kV/30mA, scan mode continuous/speed-3°20/min). Thermo gravimetric and differential thermal analyses (TG/DTA) of the fly ashes were performed up to 1000°C with a heating rate of 10°C/min, in a simultaneous TG/DTA (STA 409 EP). The sieved fly ashes were dried at 120°C before performing the thermal analysis (TGA/DTA). The chemical composition of the fly ashes was studied by X-ray fluorescence spectroscopy (XRF). The pozzolanicity of the ashes was determined using modified Chapelle test [Raverdy et al., 1980]. This test consisted of placing 1.000 g of mineral admixture and 1.000 g of calcium oxide in a water volume of 250.0 ml. The solutions were kept for 16 h in an oven at 85°C. At the end of the period, the CaO content was determined for titration with hydrochloric acid (HCl) solution and using phenolphthalein as indicator. The results were expressed in terms of fixed CaO, which is equal to the difference between 1.000 g and the mass of CaO obtained from titration.

Expansion Testing

The cement mortars were prepared meeting ASTM C 1260/ASTM C1567 specifications with a CEM I 42.5 R cement type, a water/binder (W/B) ratio of 0.47 and binder/aggregate (B/A) ratio of 0.44 (weight ratios). A blend of 20% of each biomass fly ash and 10% metakaolin was also tested. The components were weighed and mixed thoroughly in a laboratory mixer using a super-plasticizer to keep up the workability. This was measured with a flow table and plasticizer content was decided in order to keep a similar workability, around 120-130 mm spread diameter in all the samples. Table 1 shows the mortars formulations.

Sample	Biomass fly ash (%)	Metakaolin (%)	Superplasticizer (% of binder used)			
Reference	0	0	0			
20 F1	20	0	1			
30 F1	30	0	2			
20 F1+ 10M	20	10	2			
20F2	20	0	1.4			
30F2	30	0	2.4			
20F2+10M	20	10	4			

Table 1. Mortar formulations (W/B =0.47, B/A= 0. 44).

A potentially reactive fine aggregate (siliceous sand) with a granular range from 0.15 mm to 4.75 mm was used in this study. Fly ash replacement levels selected were 20% and 30% in weight of cement. Three mortar bars of dimensions 275 mm x 25 mm x 25 mm in size were made for each mix.

Immediately after casting, the moulds were covered and placed in a moist curing room at $23^{\circ}\pm 2C$ and Relative Humidity (RH) >95%. After 24 h the mortars were removed from the moulds and the initial expansion readings were taken using a digital length comparator accurate to 1 μ m. After this the mortars were preconditioned for 24 h in water maintained at $80\pm 2^{\circ}C$ during 24 h. The length of the mortar bars were measured and then the bars were immediately transferred to storage containers filled with 1N NaOH solution maintained at $80\pm 2^{\circ}C$. Length of the mortar bars were periodically measured over a 28 day period.

At the end of accelerated mortar-bar tests, the mechanical strength was evaluated by compression and flexural tests carried out according to EN 1015-11:1999, using a Standard Universal Testing Machine (Shimadzu). The prisms were first mechanically tested in three-point bending mode, after which each part was tested in compression.

Results and Discussions

Materials Characterisation

The main components in mineral composition by XRD in the F1 and F2 biomass fly ashes were quartz and calcite. The XRF analysis and TG/DTA analysis confirmed these results. Two major variations in temperature were seen in the TG/DTA in the range of 300° C- 600° C and at around 800° C in both ashes, indicating the presence of organic matter and calcite (Figure 1). The organic combustion of wood materials occurs in the range 300° - 600° C and the decomposition of CaCO₃ (calcite) at 800° C. The modified Chapelle test showed a CaO fixation of 618 mg/g and 701 mg/g for the biomass fly ashes F1 and F2, respectively, indicating the significant pozzolanic nature of the biomass fly ashes. The physical and chemical characterizations of the materials used in the tests are

summarized in Table 2. The difference in combustion technology used in the plants influenced the chemical properties of the biomass fly ashes. The fly ashes were similar to a class C material (EN450).



Figure 1. TG/DTA of biomass fly ashes a) F1 and b) F2 respectively.

Composition	Cement (%)	Biomass fly ash F1 (%)	Biomass fly ash F2 (%)	Metakaolin (%)
SiO ₂	19.74	52.10	25.10	54.66
Al ₂ O ₃	4.74	13.30	0.07	37.98
Fe ₂ O ₃	2.69	12.10	5.18	1.22
CaO	63.54	15.90	40.10	0.01
MgO	2.42	3.31	6.63	0.05
SO ₃	3.11	0.45	0.71	0.02
K ₂ O	0.62	4.14	2.07	0.01
Na ₂ O	0.08	1.05	3.61	0.01
$TiO_2 + P_2O_5$		2.57	2.64	
Loss on Ignition	1.66	10.35	3.50	0.94
Cl		0.10	0.40	
BET		28.56 m ² /g	1.74m ² /g	
Particle size		<50 μm (mean diameter 17.15 μm)	< 50 µm (mean diameter 21.32 µm)	<45 µm (mean diameter 6.03 µm)

Table 2. Physical properties and chemical analysis of raw materials.

Accelerated Expansion test

Accelerated expansion results for the mixes presented in Table 3 are shown in Figure 2. The 14 and 28 days expansion are also shown in Table 3. According to the ASTM C 1260 test-method, an aggregate is considered reactive if the average expansion of the three bars of mortars at the end of 14 days of immersion in NaOH is greater than 0.20%. The expansion of the reference mortar prepared with the OPC CEM I type was 0.31% at 14 days and 0.51% at 28 days. This confirms the high reactivity of the aggregate used in these experiments.

Table 3. Expansion results at 14 and 28 days according ASTM C 1260/ASTM C 1567 method.

Sample	Expansion (%)			
	14 days	28 days		
Reference	0.30	0.51		
20F1	0.25	0.39		
30F1	0.23	0.35		
20F1+10M	0.03	0.06		
20F2	0.24	0.37		
30 F2	0.21	0.31		
20F2+10M	0.06	0.11		



Figure 2. Expansion curves for the reference and the fly ash containing mortars.

The expansion results for mortar mixtures containing 20% and 30% biomass fly ash showed a distinct reduction in the expansion compared to the plain cement mortars. It was observed that the expansion

rate of biomass fly ash mortars was high in the initial stages and after that it seems to decrease. This can be due to the limited pozzolanic reactions resulting in a marginal reduction in expansion until pozzolanic reaction starts to influence the microstructure development and pore solution composition [Xu, 1995]. However, the expansion values for the biomass fly ashes were more than 0.2% and 0.3% at 14 days and 28 days, respectively. The addition of metakaolin in the blend with biomass fly ash did a significant improvement in the expansion results, indicating the effective use of biomass fly ash along with metakaolin in mitigating the ASR. The metakaolin was much effective in inhibiting the ASR even when used at lower rates of cement replacement than the biomass fly ash. The greater relative effectiveness of metakaolin when compared to the biomass fly ash is likely related to its smaller particle size and primarily alumina-siliceous chemical composition which results in its greater reactivity [Silva *et al.*, 2010, Moser *et al.*, 2010]. The 20B+10M blend mortars show a mixed behaviour of both metakaoline and biomass fly ash.

Table 4 shows the flexural and compressive strength of the mortars in terms of the content of the biomass fly ash and metakaolin after expansion tests. An improvement in the flexural strength was noticed in the metakaolin blended with biomass fly ash mortars compared to biomass fly ash cement formulations. 30F1 fly ash showed the maximum compressive strength, where as 30F2 showed the minimum compressive strength. The strength properties can be influenced by the compactness of the mortars, the amount of the hydrated materials and the additives used in the mortar preparations. The total water content was kept constant in all the mortars. It was observed that variation in densities caused the variation in the mortar strength. Fly ash F1 was finer than Fly ash F2 that in turn affected the compactness of the mortars. Currently, the concrete prism expansion tests according the RILEM AAR-3 and RILEM AAR-4 test methods are being done to confirm the good response of biomass fly ash in mortar-bar tests.

Sample	Flexural Strength (MPa)	Compressive Strength (MPa)	Density (g/cm ³)
20F1	4.16	46.08	2.53
30F1	4.50	50.19	2.63
20F1+10M	7.28	41.81	2.30
20F2	3.63	42.45	2.25
30F2	3.57	32.20	2.05
20F2+10M	6.34	36.36	2.07

Table 4. Mechanical Strength properties of expansion tested mortars.

Conclusions

Accelerated mortar-bar tests were conducted according to ASTM C1260/ASTM C1567 to evaluate the behavior of the biomass fly ash in the ASR inhibition mechanism. Two biomass fly ashes having slightly different chemical compositions were used for the evaluation tests. The fly ashes were pretreated by sieving at 75 μ m and were also subjected to a leaching process in order to remove the excess soluble salts.

The mortars were made with 20% and 30% of biomass fly ash substitution of cement in weight. A blend of 20% biomass fly ash and 10% metakaolin was also tested. The results obtained have shown a clear reduction in expansion due to ASR in the biomass fly ash mortars. Further investigation is in progress on concrete prisms made of biomass fly ash replaced cements to confirm the results obtained in mortars.

Acknowledgments

The authors wish to acknowledge Fundação para a Ciência e Tecnologia (FCT) for the financial support under project EXREACT (PTDC/CTM/65243/2006) and PhD grant SFRH/BD/32500/2006.

References

ASTM C 1260, 2001, "Standard test method for potential alkali reactivity of aggregates (mortar-bar method)", *ASTM International*, West Conshohocken, United States, 5.

Dockter B.A., 2009, "Using class C fly ash to mitigate Alkali silica reaction in concretes", 2009 *World Coal Ash (WOCA)*, May 4-7, Lexington KY, USA, (www.flyash.info)

Dockter B.A., Eyelands K.E., 2003, "Development of management options for biomass combustion by products", *International Ash Utilization Symposium*, Centre for Applied Energy Research, University of Kentucky, paper no.82.

Hester D., McNally C., Richardson M., 2005, A study of the influence of slag alkali level on the alkali–silica reactivity of slag concrete, *Construction and Building Materials* (19), 661–665.

Ichikawa T., 2009, "Alkali-silica reaction, pessimum effects and pozzolanic effect", *Cement and Concrete Research*, (39), 8, 716-726.

Lane D.S., Ozyidirim C., 1999, "Preventive Measures for Alkali Silica Reactions (binary and ternary Systems)", Cement and Concrete Research, (29), 1281-1288.

Maciejewska A, Veringa H., Sanders J., Peteves S.D., 2006, "Co-firing of biomass with coal: Constraints and role of Biomass pre-treatment", *European commission Directorate General*, Joint Research Centre, EUR22461 EN.

Malvar L. J., Lenke L. R., 2006, "Efficiency of fly ash in mitigating Alkali Silica Reaction based on Chemical Composition", *ACI Materials Journal*, (103),5, 319-326.

Moser D. R, Jayapalan A, R., Garas V.Y., Kurtis, K E., 2010, "Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali Silica Reaction Mitigation in Concrete", *Cement and Concrete Research*, 4 (40), 1664-1672.

Rajamma R., Ball R.J., Tarelho L.A., Allen G.C., Labrincha J.A., Ferreira V.M., 2009, "Characterization and use of biomass fly ash in cement-based materials", *Journal of Hazardous Materials*, (172), 2, 1049-1060.

Raverdy M, Brivot F, Paillère AM, Bron R. 1980, Appréciation de l'activité pouzzolanique de constituents secondaires. In: Proceedings of *7e Congrés International de la Chimie des Ciments*, Paris, France; p. 6–41.

Silva, A. S., Soares, D., Matos, L., Salta M., Divet, L., Pavoine, A., Candeias A., Mirão, J., 2010, "Influence of Mineral addition in the inhibition of delayed Ettringite formation in cement based Materials – A Microstructural Characterization", *Materials Science Forum*, (636-637), 1272-1279.

Wang S., Baxter L., 2007, "Comprehensive study of biomass fly ash in concrete: Strength, microscopy, kinetics and durability," *Fuel Processing Technology*, (88), 11, p. 1165-1170.

Xu G.J. Z., Watt D.F., Hudec P.P., 1995. "Effectiveness of mineral admixtures in reducing ASR expansion", *Cement and Concrete Research*, (25), 6, 1225-1236.