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Activated Coal Fly Ash as Improved Mineral Addition in Cement and Concrete

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ABSTRACT

A laboratory investigation on the use of coal fly ash (FA) with coarse grain size and high LOI as pozzolanic material for the production of cement mortars was carried out. To that aim the FA was grinded by means of a planetary ball mill until a size distribution similar to silica fume and its LOI was reduced in a triboelectrostatic separator. Some basic properties (i.e., workability, setting times and mechanical strength) of mortars with Portland cement or sand substituted by micronized or beneficiated micronized FA or silica fume were comparatively evaluated. Based on the experimental results, a consistent chemico-mechanical improvement of such FA was achieved, making their use in high strength cement conglomerates profitable.

INTRODUCTION

Cement concrete is undoubtedly the most widely used construction material in the world. *Silica fume* (SF, also known as microsilica, a byproduct of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys) consists of very fine vitreous particles with a surface area ranging from 13,000 to 30,000 m^2/kg, with diameter approximately 100 times smaller than the average cement particle. In spite of its industrial waste origin, thanks to its extreme fineness and high silica content SF has become the most valuable by-product among pozzolanic materials [ACI Committee, 1987]. Appa Rao [2003] pointed out that mortars with SF content in the 20÷25% range develop the highest compressive strength at a curing age of 28 days and that both initial and final setting times decrease with increasing SF content.

Coal fly ash (FA) - a waste resulting in immense amount worldwide, deriving from the combustion of coal in thermal power plants, made mainly by vitreous (amorphous) alumina silicate with a small amount of crystalline minerals – is also used as a pozzolanic substitute in concrete, although less profitably than SF. Chindapraisirta et al. [2004] found that mortars with fine rather than coarse FA require less water. Gengying et al. [2005] showed that cement substitution with FA increases the compressive strength by a reverse proportionality to its mean particle diameter, especially at the age of 28, 56 and 120 days. While confirming that the highest compressive strength of FA-substituted mortars depends primarily on the size of the FA embedded, Burak et al. [2009] demonstrated that increasing the fineness may cause higher mixing water demand due to the increase in surface area of the FA particles. Quite often, however, excessive unburned carbon residue (i.e., when the LOI, Loss On Ignition, exceeds 5%) and improper surface characteristics make FA no longer appealing for the cement & concrete industry. The well known mechano-chemistry [Boldyrev, 1983] and electro-chemistry [Stencel et al., 1998] tribo-techniques may be applied in order to modify the surface structure and the average size and to reduce the LOI of the FA when necessary.

The purpose of the present study was to investigate comparatively the utilization of SF as well as mechanochemically micronized fly ash (MFA) and electrochemically beneficiated micronized fly ash (BMFA) for potential cement replacement in high strength concrete.

MATERIALS AND METHODS

Materials

FA samples from ENEL power plant in Brindisi (Italy's largest carbon fuelled power plant) as well as commercial Portland cement (PC) and silica fume were used.

Mechanical activation

FA was grinded using a Fritsch Pulverisette 6 laboratory planetary mill under the following operating conditions: rotation speed 450 rpm; mass to be milled 20 g per cycle; milling-to-milled mass ratio 10:1; grinding ball diameter 5 mm; grinding time 4 hr; volumetric mill filling factor 30%. The milling treatment was occasionally stopped for few minutes to avoid excessive temperature increase. Further details have been provided elsewhere [Cangialosi et al., 2007].

Tribo-electrostatic activation

The micronized FA was also beneficiated (i.e., its LOI content was decreased) by means of the triboelectrostatic separation technique using a laboratory apparatus (TFS, Kentucky, US) with the process scheme shown in Figure 1, already described elsewhere [Cangialosi et al., 2006]. In practice, collision among the solid particles and with the walls of the spiral conduct (*charger tube*) during the pneumatic transport of the FA builds up opposite electrostatic charge on its inorganic (*ash*) and organic (*carbon*) fractions, which can thus be easily split by an electric field (*high voltage power field*) and collected separately (*cyclones*). The resulting *ash* fraction hence exhibits a lower LOI value (*beneficiated FA*), correspondingly increased in the *carbon* fraction.

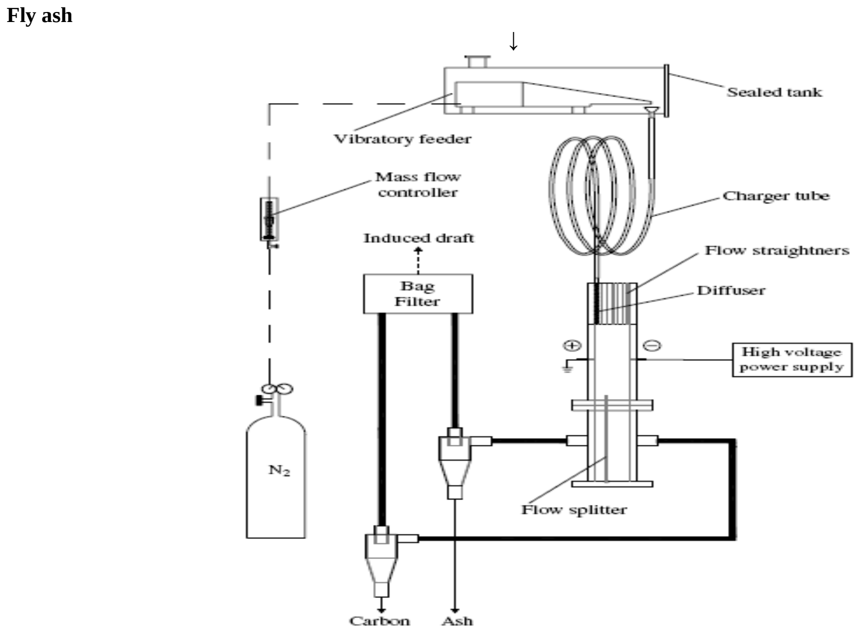

Fig. 1. Process Scheme of the Tribo-electrostatic Separator Employed

As shown in Tab.1, the chemical composition of FA didn't change with the mechano-chemical activation, resulting just in its structural change (crystalline to amorphous transition, smaller particle diameter), while the tribochemical beneficiation of MFA decreased its LOI from ≥7 to ≤4%.

Table 1. Physico-chemical Characteristics of the Investigated Materials

Material	$Ø_{avg}$ (μm)	Content (% in weight)							
		LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
PC	40	1.67	17.6	5.05	3.75	56.2	14.7	0.35	0.68
SF	0,5	4.36	86.37	0.39	1.9	5.29	0.96	0.17	0.56
FA	40	7.04	47.75	29.16	8.08	5.93	1.48	0.18	0.38
MFA	20	7.04	47.75	29.16	8.08	5.93	1.48	0.18	0.38
BMFA	20	3.97	49.33	30.12	8.35	6.13	1.53	0.19	0.39

(PC Portland cement; SF silica fume; MFA micronized fly ash; BMFA beneficiated micronized fly ash)

Mix design

A first series of mortars (Mixes A) was made by three types of mixtures of PC and one of the by-products tested in this work (i.e., PC/SF, PC/MFA and PC/BMFA); the cement substitution ratio was between 10 and 25% in weight. Using this same ratio, in the second series (Mixes B), the three by-products were used to substitute sand. Water-to-binder ratio (w/b) was 0.4 in mixes A and 0.35 in mixes B. A total of 26 mixes were tested accounting also for the reference one (Mix 1, with 100% PC and 0% by-products).

Sample preparation and testing procedure

Mixes containing the blends investigated were prepared according to UNI EN 197-1 and UNI EN 196 procedures. Setting time and water demand were evaluated on the fresh mixes (pastes) No.1, 3A, 5A and 7A (i.e., those with highest cement substitution). The hardened mix (mortars) for each sample was prepared using three 40 x 40 x 160 mm moulds filled and compacted using a vibrating table. The moulds were cured for 2, 7 and 28 days for compressive strength, measured as the average of 3 specimens. The setting time of pastes was measured with a Vicat apparatus.

RESULTS AND DISCUSSION

It is well known that during the mechanochemical activation the solid particles of FA undergo a large number of inter/intra collisions which modify their surface properties by creating microdefects, increasing their surface energy, chemical reactivity etc. [Boldyrev, 1993]. In particular, although single micronized particles would exhibit higher specific surface, they tend to form clusters with overall (bulk) lower surface.

It is also well known that during the tribo-electrochemical beneficiation, further inter/intra collisions among the particles build up positive and negative electrostatic charges on the MFA mineral and carbonaceous fraction respectively, which then can be easily separated by an electric field in order to yield a FA with reduced LOI [Stencel et al., 2003].

Figure 2 compares the water demand of mortars with 25% substitution of Portland cement by the by-products investigated. It can be seen that the water demand increases remarkably (≥33%) when Portland is substituted by raw FA (Mix 3A) due to its high irregular surface. This no longer occurs when Portland is substituted both by MFA (Mix 5A) or BMFA (Mix 7A), whose bulk surface has been reduced by micronization.

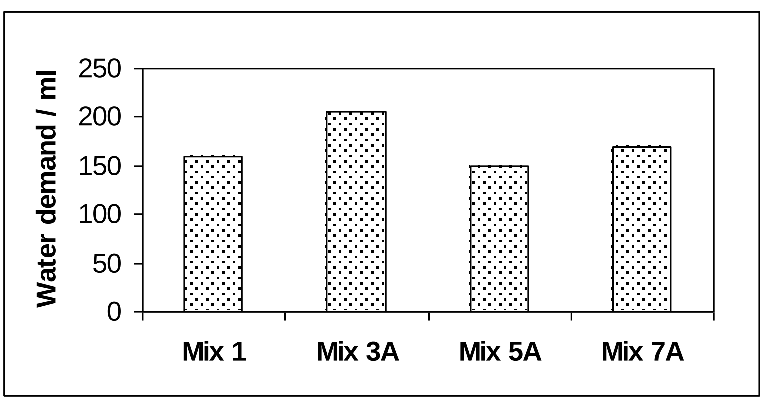

Fig. 2. Water Demand in Mixes with 0% (1) and 25% Substitution of Portland Cement with FA (3A), MFA (5A) and BMFA (7A)

As shown in Figure 3, both initial and final setting times of all substituted mixes are shorter than the unsubstituted one (Mix 1). This must be kept in mind as the setting time represents the time available for transportation and placement of the paste.

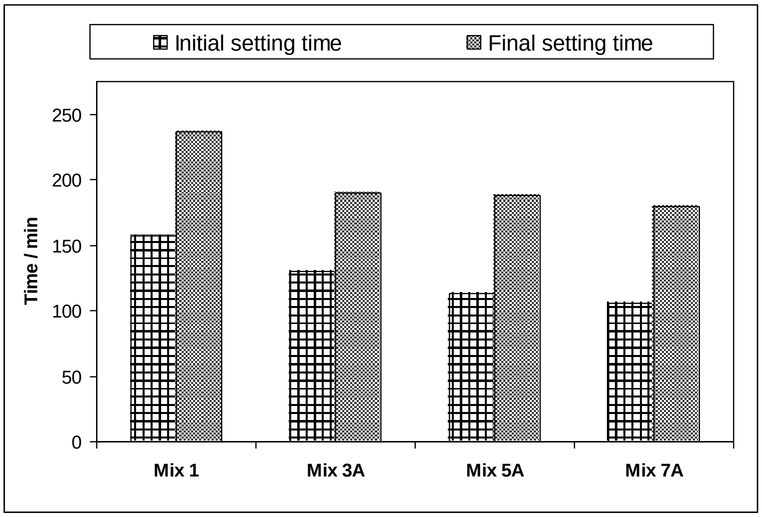

Fig. 3. Initial and Final Setting Times in the Investigated Pastes

Figure 4 compares the increase of compressive strength at 0.40 or 0.35 water-to-binder ratio when up to 25% Portland cement is substituted by the three by-products. From these results it clearly appears that after 28-days for all the by-products at both w/b ratios investigated:

1. substitution of Portland cement proved always beneficial
2. 10% is better than 25% substitution
3. substitution is more effective at 0.35 than 0.40 w/b ratio
4. compression strength increased in the order: none < SF < MFA < BMFA substitution.

It may be concluded, accordingly, that coal fly ash properly treated (i.e., with LOI ≤4% and mean diameter ≤20 μm) may ensure stronger 28-days compressive strength than silica fume when used to substitute up to 25% Portland cement.

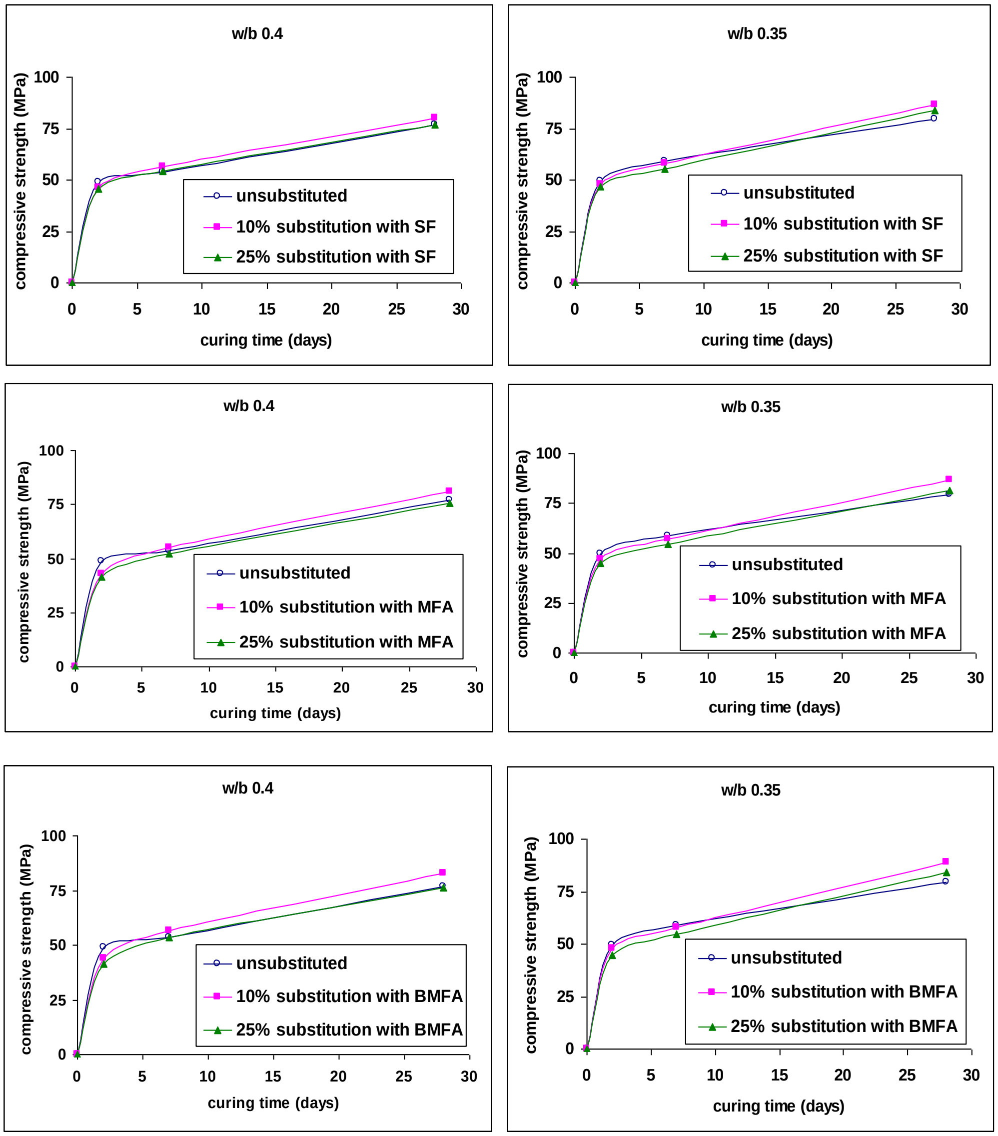

Fig. 4. Compressive Strength with Curing Age for Substitution of Portland Cement

Figure 5 compares the increase of compressive strength at w/b 0.40 or 0.35 when the three by-products substitute up to 25% of sand. As already commented for the data in Figure 4:

1. substitution of sand proved always beneficial
2. 25% is always better than 10% substitution
3. substitution is more profitable at 0.35 than 0.40 w/b
4. compression strength increased in the order: none < SF < MFA < BMFA substitution.

Properly treated FA exhibited better attitude than silica fume also for substituting the sand.

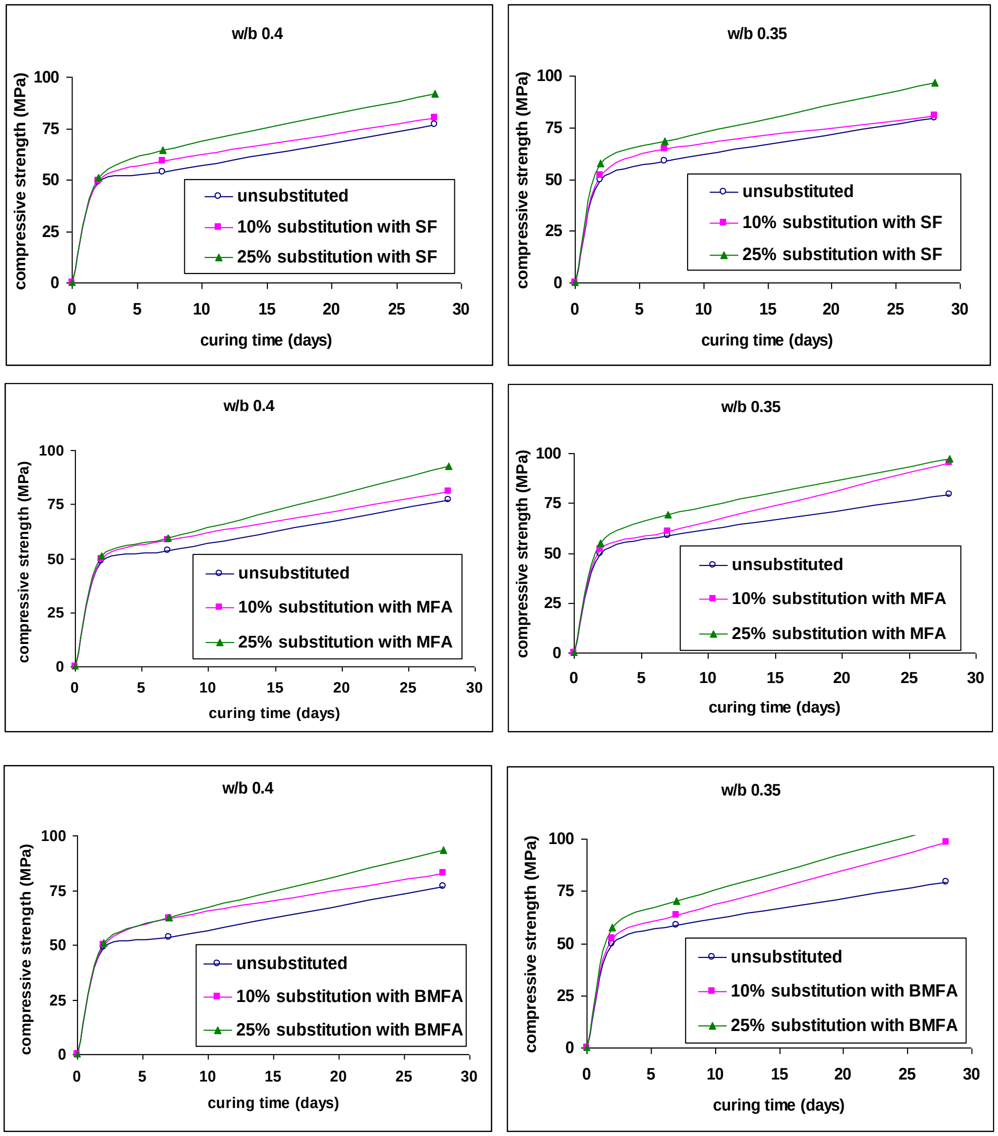

Fig. 5. Compressive Strength with Curing Age for Substitution of Sand

In order to obtain a comprehensive evaluation of the benefits achievable when the three by-products investigated are used as cement substitutes, the previous results have been rearranged in terms of a Performance Index (I_p) defined as follows:

$$I_p = F_s + F_t + F_w$$

where F_s (compressive strength factor) is the ratio between the 28-days compressive strength of each mix and the nominal strength of the Portland cement used (52.5 MPa), F_t (initial setting time factor) and F_w (water demand factor) are the ratio between the corresponding figure of each mix and the non-substituted one.

As shown in Figure 6, it may be comprehensively stated that in the experimental conditions investigated for all the three by-products:

1. substitution of ≤25% Portland or sand was always beneficial
2. 25% is better than 10% substitution
3. properly treated FA exhibits better substituting attitude than silica fume.

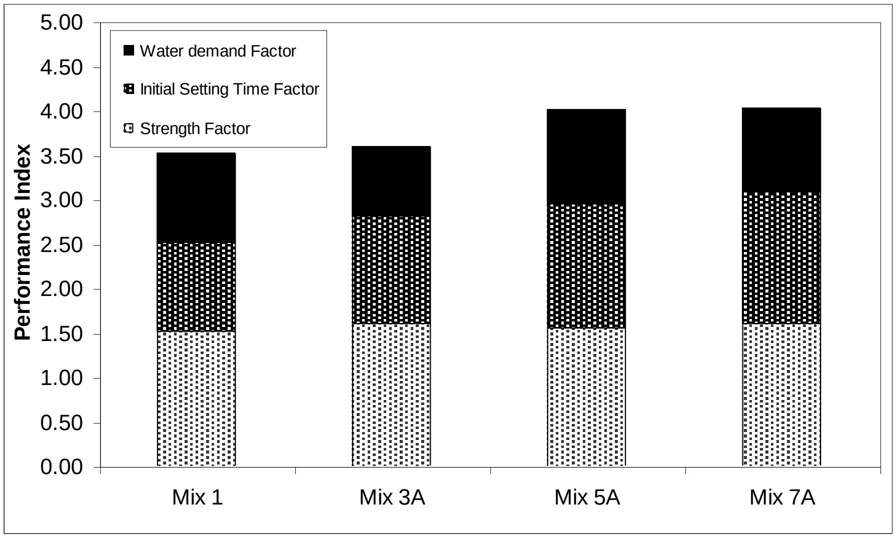

Fig. 6. Performance Index for Some Investigated Mix Design (w/b 0.35)

It may be conclusively stated that substitution of Portland and/or sand either by raw or, preferably, by properly treated FA always yields better mixes, showing higher strength, requiring least water and least setting time.

CONCLUSIONS

Nowadays increasing amount of coal fly ash worldwide exhibits chemical (i.e., excessive unburned residue) and/or physical (e.g., excessive size) characteristics which no longer allow its profitable use by the cement & concrete industry. Such FA, however, may be properly treated with well known advanced tribo-techniques such as *mechanochemistry* and/or *electrochemistry* to yield micronized (MFA) and/or beneficiated micronized (BMFA) fly ash respectively.

The present investigation has shown that both MFA and BMFA may be conveniently used to substitute up to 25% of Portland cement and/or sand thus achieving better properties (i.e., higher compressive strength and lower water demand and setting time) than unsubstituted and even silica-fume-substituted concrete specimens.

Further experiments are planned to assess the overall economic feasibility of the treatment in the preparation of high strength cement conglomerates. In particular, the cost-effectiveness of substituting Portland cement by just electrochemically beneficiated (BFA), not by mechanically activated (MFA) or electrochemically *and* mechanically activated (BMFA), fly ash will be evaluated in order to avoid the expensive energy-consuming grinding treatment.

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REFERENCES

ACI Committee 226. 1987b. Silica fume in concrete: Preliminary report. ACI Materials Journal March-April: 158-66

Appa Rao G. (2003), Investigations on the performance of silica fume-incorporated cement pastes and mortars, Cement and Concrete Research 33 (2003) 1765–1770

Boldyrev V.V., (1983) Experimental methods in the mechanochemistry of inorganic solid. Treatise on materials science and technology, 19, H. Herman ed., Academy Press, 1983

Boldyrev V.V., (1993) Mechanical activation of solids, 1st Intern. Conf. on Mechano-chemistry, InCoMe 93, Kosice (Slovak Republic), 23-26 March 1993

Burak F., Selçuk T., Hasan K., (2009) Optimization of fineness to maximize the strength activity of high-calcium ground fly ash – Portland cement composites, Construction and Building Materials 23 (2009) 2053–2061

Cangialosi F., Notarnicola M., Liberti L., Caramuscio P., Belz G., Gurupira T.Z., Stencel J.M., (2006) Significance of surface moisture removal on triboelectrostatic beneficiation of fly ash, Fuel 85 (2006) 2286-2293

Cangialosi F., Intini G., Liberti L., Notarnicola M., Pastore T., Sasso S., (2007) Mechano-chemical treatment of contaminated marine sediments for PAHs degradation, Chem. Sustain. Develop. 15 (2007) 139-145

Chindaprasirta P., Homwuttiwongb S., Sirivivatnanon V., (2004) Influence of fly ash fineness on strength, drying shrinkage and sulfate resistance of blended cement mortar, Cement and Concrete Research 34 (2004) 1087–1092

Gengying Li, Xiaozhong Wu, (2005) Influence of fly ash and its mean particle size on certain engineering properties of cement composite mortars, Cement and Concrete Research 35 (2005) 1128–1134

Stencel J.M., Schaeffer J., (1998) Method and apparatus for triboelectric-centrifugal separation, U.S.Pat.No.5755333, 26 May 1998

Stencel J.M., Gurupira T.Z., (2003) Particle separation/purification system, diffuser and related methods, U.S.Pat.No.213729, 20 November 2003

UNI EN 196: Methods of testing cement: 1). Determination of strength; 2) Chemical analysis of cement; 3) Determination of setting time and soundness

UNI EN 197-1: Composition, specification and conformity criteria for common cements