Valorization of non-conventional fly ashes in eco-efficient cements

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Abstract. The aim of this project was to evaluate the potential of coal fly ash coming from a spreader stoker power plant (Reunion Island) to be used in cement-based materials. Actually this fly ash cannot be considered equivalent to pulverised coal fly ash regulated by EN 450-1, but its reuse could represent a real progress for the sustainable development of the island. This feasibility study is divided into three parts: 1- characterization of raw and treated fly ashes, 2- evaluation of the activity of the ashes in cement-based materials, and 3- fabrication of laboratory CEM II containing treated fly ashes. The results show that spreader stoker fly ash has properties similar to those of standard fly ash, except for the high unburned carbon content. The pozzolanic activity of raw and treated ashes is notable, leading to high strength activity indexes. However, rheological properties and setting time delays still need to be assessed. Laboratory CEM II cements made using the treated ashes gave superior mechanical performance when compared to CEM II containing typical constituents (clinker and natural pozzolana) usually found in Reunion Island

1 Introduction

The use of by-products in the manufacture of composite cements has been known for a long time. For instance, fly ash, blast furnace slag and silica fume are used all over the world in partial replacement of clinker [1]. However, the use of these by-products is usually regulated, as is the case in Europe with the standard EN 197-1 [2]. For now, it is not possible to use just any kind of by-products and permitted ones must comply with specifications stating physical and chemical requirements, e.g. loss on ignition, free lime content, fineness, activity index, etc. [3].

On the one hand, local situations sometimes exist where non-standard by-products could be used, although they are outside the normalized range. Such is the case for Reunion Island, a small French island (2512 km^2) which produces a few thousand tons of coal fly ash in its spreader stoker power plants. These ashes are currently sent to landfills since they do not comply with EN 450-1, a standard covering only fly ash obtained from the burning of pulverized coal.

On the other hand, Reunion Island has no cement plants. Clinker imported from other countries is ground locally and mixed with a natural pozzolana to manufacture CEM II cements. Use of the ashes produced locally could mean real progress for the sustainable development of the island, since their rational valorization could decrease the amount of clinker to be imported.

The aim of this paper is to report a feasibility study on the reuse of spreader stoker coal fly ash in the manufacture of composite cement. The study is divided into three parts: a characterization of the ash, an evaluation of its reactivity, and manufacture, at a laboratory scale, of composite cements. Three fly ashes from the same plant were studied: the raw ash and two ashes treated to lower their unburned carbon contents.

2 Materials and methods

2.1 Materials

Laboratory grade portlandite was used to evaluate the pozzolanic reactivity of the ashes. The cement used for the evaluation of the performance of fly ashes in cement-based materials was a CEM I 52.5 R, according to EN 197-1. Clinker, gypsum and natural pozzolana from Reunion Island were used to manufacture the laboratory cements with and without fly ash. The siliceous sand was in conformity with EN 196-1 [4].

The raw fly ash was produced in a power plant which uses a spreader stoker type calciner. For half the year, the plant burns bagasse and produces bagasse ashes, which are already reused in other applications. For the rest of the year, coal from South Africa is burned in the plant, producing the ash that is then landfilled.

In order to reduce the unburned carbon remaining in the ash, the by-product was treated following two main processes: carbon burn out (CBO) at 1000°C and tribo-electrostatic separation (TRE).

2.2 Methods

The main characteristics investigated were:

- loss on ignition (EN 196-2) [5]
- specific gravity by hydrostatic weighing
- specific surface area (Blaine) (EN 196-6) [6]
- particle size distribution by laser granulometry (CILAS 1090 LD)
- morphology by SEM and EDX
- mineralogy by X-ray diffraction (Siemens D5000)

The reactivity of the ashes was found by measuring the portlandite consumption by thermogravimetric analysis (STA 449 F3 Jupiter). The mixtures were composed of 1 part portlandite, 4 parts fly ash and 3 parts water. The pastes were cured at 20°C in sealed plastic tubes.

The tests on cement pastes and mortars (EN 196-1) with ashes included:

- normalized consistency on paste (EN 196-3) [7]
- setting time on cement paste (EN 196-3)
- mortar flowability (NF P 15-437) [8]
- semi-adiabatic Langavant calorimetry (EN 196-9) [9]
- compressive strength (EN 196-1)

The mixtures containing the fly ashes were composed of 75% of cement and 25% of fly ash. All water-binder ratios were set at 0.50, except for the consistency and setting time tests carried out on pastes (variable W/B).

The laboratory cements were ground in a planetary ball mill with ceramic balls. Because of the small amount of binder produced, the mortars (same composition as in EN 196-1) were cast in 2x2x2 cm moulds. Each compressive strength result was the mean of 12 replicate values.

3 Results

3.1 Characterization

Table 1 gives the loss on ignition (LOI), specific gravity, specific surface area and mean diameter of all three fly ashes. It can be seen that the raw fly ash LOI was quite high, due to the lack of efficiency of the burning process. The small size of the power plant and the difficulty in optimizing the burning process were probably responsible for this result. This high carbon content could lead to high water demand, efflorescence on concrete and reduced efficiency of organic admixtures (e.g. air entraining agent). The CBO or TRE treatments were quite efficient in reducing the unburned carbon content.

The high specific surface area (SSB) could be partly explained by the high porosity of unburned carbon, but also by the presence of very fine particles in the ashes (see, for instance, Figure 1c). The decrease of SSB in the case of CBO might be related to an agglomeration of small particles when the ash was heated.

Table 1. Characteristics of raw and treated fly ashes

	LOI	SG	SSB	D50
Raw	27.9	2.19	7900	15
CBO	3.9	2.44	5900	14
TRE	7.2	2.28	8200	11

LOI: Loss on ignition (%); SG: Specific gravity (g/cm^3); Specific surface Blaine (cm^2/g); D50: 50% passing (µm)

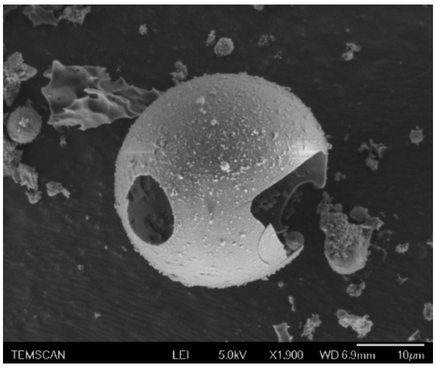
XRD measurements (not presented here) showed that this fly ash had a polyphasic structure composed of an amorphous phase and several crystallized phases, such as mullite, quartz, feldspars and hematite. These minerals are similar to those usually encountered in normalized fly ash from the pulverized coal process [10]. The presence of an amorphous phase mainly composed of silica and alumina guarantee a certain reactivity with portlandite, as shown later.

The treatment of the raw fly ash to produce CBO and TRE did not modify the mineralogy of the by-product since the same minerals were found in both treated fly ashes (except for TRE which no longer contained hematite). Only the quantity of the amorphous phase seemed to decrease in the case of carbon burn out (CBO), probably due to the heating of the ash, which may have led to a recrystallization of this phase. It could be more interesting to cool the ash rapidly after CBO treatment in order to maintain the amorphous phase intact.

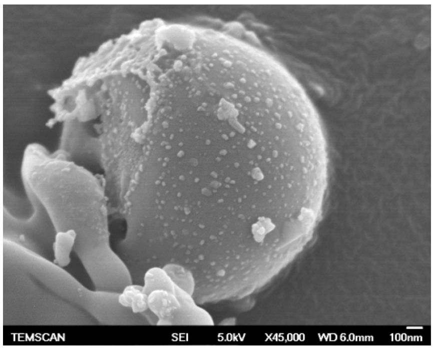
Figure 1 shows that some fly ash particles presented a rounded shape similar to the one found in fly ash from the pulverized coal process. The particle size ranged from less than 1 µm to more than a few tens of µm. EDX analysis of the spherical particles showed that SiO_2 + Al_2O_3 + Fe_2O_3 always made up more than 80% of the total.

However, several particles having an irregular form were also seen in all three fly ashes. This was especially the case for the raw fly ash, since it contained a high proportion of unburned carbon. The corresponding particles were usually more porous than the others, thus leading to a high water demand when used in cement-based materials (see results later).

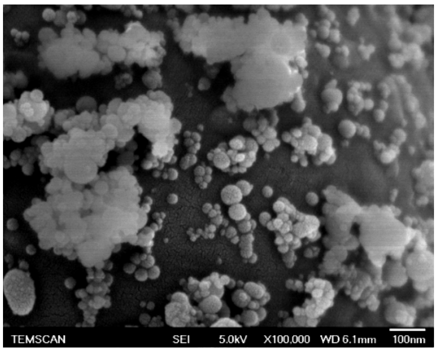
In the case of CBO, the spherical particles were less frequently seen and the shape was sometimes more irregular, probably due to a partial fusion of the particles during the thermal treatment. For TRE fly ash, numerous small spherical particles were easily found, while the porous irregular particles were rare. This was in accordance with the LOI of this ash.



(a) raw fly ash



(b) CBO



(c) TRE

Fig. 1. Morphology of fly ashes (SEM).

3.2 Activity of fly ashes

The effect of the different ashes on mortar workability was assessed by measuring the flowing time in LCL apparatus. Figure 2 shows that, compared to the reference with cement only, the use of 25% of fly ash increased the flowing time, meaning that the by-products increased the water demand of the mortars. The worst result concerned the raw fly ash, probably because its high unburned carbon content consumed more water in its high internal porosity. Although the flowing times remained longer than the reference, the treated fly ashes limited the increase in water demand.

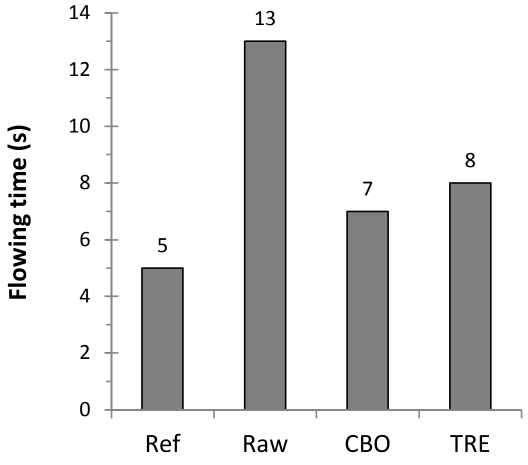


Fig. 2. Flowing time of mortars containing 25% of fly ashes compared to reference.

Table 2 confirms the increase in water demand of the ashes on cement pastes intended for setting time measurements. It can be seen that the setting times of fly ash mortars were much longer than the reference. This result could be explained by various mechanisms [11]:

- a dilution effect of the cement since the fly ash pastes contained 25% less cement than the reference, resulting in a decrease in the quantity of hydrates formed in the first few hours;
- an increase of the water-binder ratio due to the high water demand, known to have an effect on the setting time;
- a harmful effect of the ashes themselves, maybe due to the presence of minor elements (e.g. Zn, P…) perturbing the hydration of the cement [12].

These setting delays were confirmed by semi-adiabatic calorimetry measurements, as shown on Figure 3. It is seen that, compared to the reference, the use of fly ash retarded the production of heat. As for the setting times, this was especially the case for raw and TRE ashes (Table 2). CBO fly ash had a less significant effect, maybe due to its much lower carbon content (CBO treatment may help to immobilize the trace elements perturbing hydration).

The effect of the treatment was not clear, since it either increased or decreased the setting time compared to the raw ash. More research still needs to be done to explain and limit this effect, the delay being higher than what is usually permitted by EN 450-1. Nonetheless, it can clearly be seen (Figure 3) that both treated ashes had an effect on the amount of heat released at later age. It is probable that the small particles played a role of germination sites for hydrates, helping to increase the overall hydration of cement particles [13].

Table 2. Normalized consistency (expressed as W/B) and setting time of cement pastes containing 25% of fly ash compared to CEM I alone (Ref).

	W/B	Setting time (h)	EN 450-1 limit (h)
CEM I (Ref)	0.31	2.4	Ref + 2h = 4.4
Raw fly ash	0.39	5.1	
CBO	0.37	4.0	
TRE	0.38	5.9	

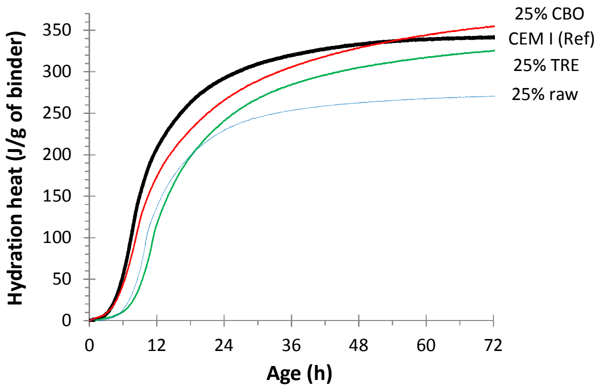


Fig. 3. Hydration heat of mortars containing 25% of fly ashes compared to reference.

In order to evaluate the pozzolanic reaction of the ashes, the consumption of portlandite was followed by TGA on portlandite + fly ash pastes. Figure 4 reports the results up to 90 days. It can be seen that all ashes presented high reactivity, since the portlandite contents were found to be significantly decreased at 7 days and over. At 90 days, less than 3% of the portlandite remained. It should be noted that the presence of unburned carbon did not seem to affect the reactivity of the ash.

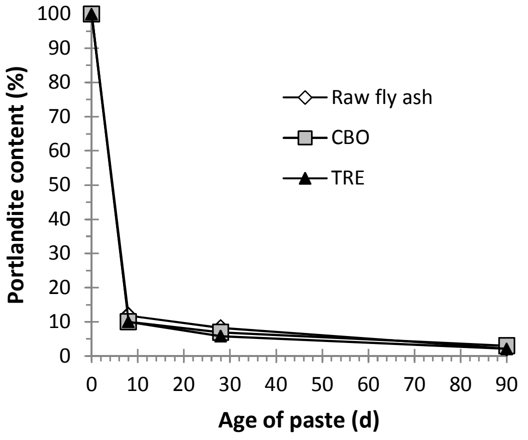


Fig. 4. Portlandite content determined by TGA of pastes composed of 20% portlandite and 80% fly ash.

Figure 5 reports the compressive strength results as strength activity index (SAI), i.e. the ratio of the compressive strengths of fly ash mortar and reference mortar. The following observations can be made:

- all the SAI values (at 7 and 28 days) were higher than the 28-day minimum value required in EN 450-1;
- SAI increased between 7 and 28 days, meaning that the pozzolanic reaction still had an effect at later age;
- as already seen for portlandite consumption, raw fly ash had a significant effect on the strength of mortars, although it contained almost 28% of unburned carbon;
- the treatment of fly ash had a positive effect on SAI, especially for TRE (selection process). CBO treatment could probably be improved by increasing the speed of cooling, thus helping to keep the amorphous phase of the ash and so increase its reactivity;
- the delay in setting time observed at young age did not seem to have a significant effect on later age strength.

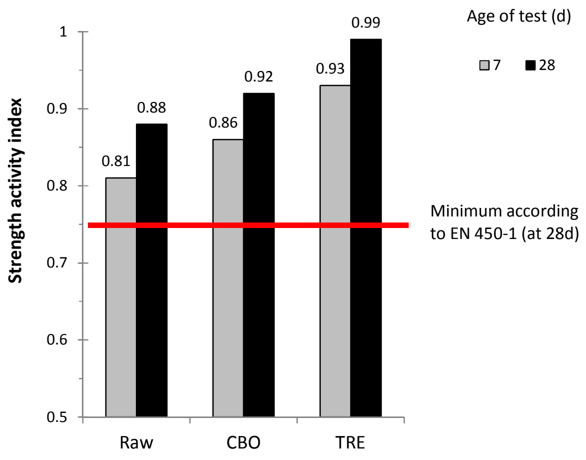


Fig. 5. Strength activity index at 7 and 28 days of mortars containing 25% of fly ashes. Comparison with the minimum requirement (0.75) given by EN 450-1.

3.3 Manufacture of cements with fly ashes

The results of the characterization showed that these ashes had a lot in common with standard pulverized coal fly ash. It was decided to manufacture CEM II cements from the treated fly ashes. Table 3 gives the compositions tested. According to EN 197-1, the maximum values of additions must be in the range 6-20% for CEM II/A and 21-35% for CEM II/B.

The clinker was first crushed, then mixed and ground with other compounds for:

- 30 minutes in the case of CEM II/A
- 15 minutes (clinker+gypsum) followed by 5 min after adding TRE fly ash for CEM II/B

Table 3. Composition of manufactured laboratory cements

	Clinker*	Poz**	Fly ash**	Gypsum
CEM II/A 42,5 N				
Ref (10% pz)	90%	10%	-	4%***
10% TRE		-	10%	
10% CBO		-	10%	
CEM II/B 32,5 N				
Ref (25% pz)	75%	25%	-	4%***
25% TRE		-	25%	

* clinker / (clinker+addition)
** addition / (clinker + addition)
*** gypsum / (gypsum+clinker+addition)

Table 4 gives the compressive strength of 2x2x2 cm cubes at 7 and 28 days for all the cements made. The main observations are:

- all cements complied with the mechanical requirements at 28 days given in EN 197-1 (Table 5); the 7-day value (32.5N) was easily reached; 2-day values still need to be assessed;
- at 7 days, all CEM II/A with CBO and TRE led to higher performance than cement containing the natural pozzolana. For the same age, the strength of CEM II/B with TRE was slightly lower than the reference with pozzolana;
- at 28 days, all cements with TRE or CBO had significantly higher strength than the references with pozzolana;
- these results seem to be related to the higher fineness of the fly ash cements (Figure 6).

Practically, these results could mean that, in order to keep an equivalent performance compared to pozzolana cements, the use of fly ash could lead to:

- a decrease of the grinding time, which could improve the energy balance of the cement manufacture;
- an increase in the fly ash content, allowing a decrease in the quantities of clinker to be imported to the island.

Table 4. Properties of cements made in the laboratory

	Blaine (cm^2/g)	Compressive strength (MPa)	
		7 days	28 days
CEM II/A 42.5 N			
Ref (10% pz)	3500	28.8	42.7
10% TRE	4900	45.6	65.4
10% CBO	4700	34.9	52.2
CEM II/B 32.5 N			
Ref (25% pz)	5150	37.6	45.8
25% TRE	5800	35.1	52.0

Table 5. Mechanical requirements of cements according to EN 197-1.

Strength class	Compressive strength MPa			
	Early strength		Standard strength	
	2 days	7 days	28 days	
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5
32,5 R	≥ 10,0	-		
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5
42,5 R	≥ 20,0	-		
52,5 N	≥ 20,0	-	≥ 52,5	-
52,5 R	≥ 30,0	-		

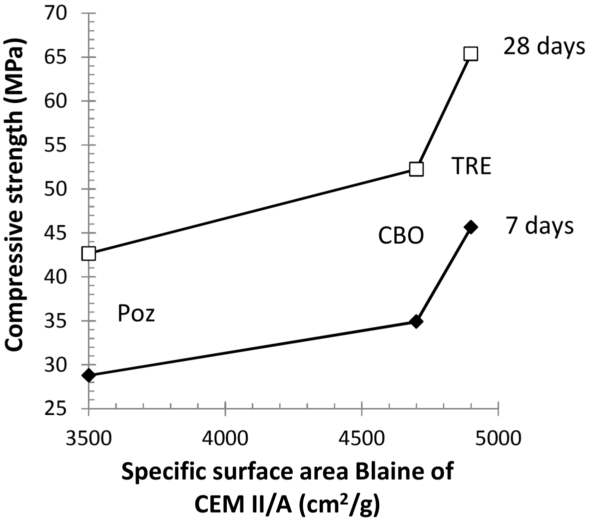


Fig. 6. Compressive strength of CEM II/A at 7 and 28 days as a function of their fineness.

4 Conclusion

The main objective of this work was to make a preliminary assessment of the valorization of spreader stoker coal fly ashes in cement-based materials. The study, divided into three parts, led to the following conclusions:

- Spreader stoker fly ash is partly composed of spherical particles, similar to those encountered in pulverized coal fly ash currently used in cements and concretes. However, the raw ash contains a large amount of unburned carbon, leading to degraded rheological properties and retarded setting time of cement-based materials. The pozzolanic reaction of the ash still remains high and the strength activity index is much higher than the minimum value specified in standard EN 450-1.

- Treated fly ashes (carbon burn out and tribo-electrostatic processes) showed significantly reduced carbon contents, and thus improved rheological and mechanical behaviour compared to raw fly ash. These ashes could probably be used in cement manufacture to replace a part of the clinker.

- Mechanical performance levels of CEM II/A and CEM II/B prepared in the laboratory from the treated ashes were superior to those obtained with CEM II containing typical constituents (clinker and natural pozzolana) usually found in Reunion Island.

References

1. F Massazza, Pozzolana and pozzolanic cements, *LEA's Chemistry of Cement and Concrete* (4th Ed, Elsevier, 2004)
2. EN 197-1, Cement. Composition, specifications and conformity criteria for common cements (2011)
3. EN 450-1, Fly ash for concrete. Definition, specifications and conformity criteria (2012)
4. EN 196-1, Methods of testing cement. Determination of strength (2005)
5. EN 196-2, Methods of testing cement. Chemical analysis of cement (2005)
6. EN 196-6, Methods of testing cement. Determination of fineness (2010)
7. EN 196-3, Methods of testing cement. Determination of setting times and soundness (2005)
8. NF P15-437, Liants hydrauliques - Technique des essais - Caractérisation des ciments par mesure de la fluidité sous vibration des mortiers (1987)
9. EN 196-9, Methods of testing cement. Heat of hydration. Semi-adiabatic method (2010)
10. E E Berry, V M Malhotra, *Fly ash in concrete* (Energy, Mines and Resources Canada, 1986)
11. M Coutand, M Cyr, P Clastres, Use of sewage sludge ash as mineral admixture in mortars, Construction Materials **159**, 153-162 (2006)
12. G Arliguie, J P Ollivier, J Grandet, Etude de l’effet retardateur du zinc sur l’hydratation de la pâte de ciment Portland, Cement and Concrete Research, **12**, 79-86 (1982)
13. P Lawrence, M Cyr, E Ringot, Mineral admixtures in mortars - Effect of inert materials on short-term hydration, Cement and Concrete Research, **33** (12) 1939-1947 (2003)