Potential application of coal–fuel oil ash for the manufacture of building materials

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Abstract

In this paper coal–fuel oil ash has been characterized in terms of leaching behaviour and reactivity against lime and gypsum in hydratory systems for the manufacture of building materials. Its behaviour was also compared to that of coal ash. Metal release was measured in a dynamic leaching test with duration up to 16 days. The results have shown that coal–fuel oil ash behaves very similarly to coal ash. The reactivity of coal–fuel oil ash against lime and gypsum was measured in mixtures containing only lime and in mixtures containing both lime and gypsum. These systems were hydrated at 25 and 40 °C under 100% R.H. The results have shown that the main hydration products are the same as those that are usually formed in similar coal ash-based systems. That is, calcium silicate hydrate in coal–fuel oil ash/lime systems and calcium silicate hydrate plus calcium trisulphoaluminate hydrate in coal–fuel oil ash/lime/gypsum systems. From the quantitative point of view, hydration runs showed that the amounts of both chemically combined water and reacted lime measured in the case under investigation are very similar to those found in similar coal ash-based systems. Finally, the measurement of unconfined compressive strength proved that the systems have potentiality for the manufacture of pre-formed building blocks.
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1. Introduction

Pulverized coal is surely one of the cheapest fuels for the generation of electric power, but it causes such problems as bridging or channelling in a hopper or choking of piping in pneumatic transportation, and it is difficult to sustain a long and stable operation of furnaces. Overcoming these difficulties to get improved and more effective operation can be achieved by means of modern combustion technology, for example turning fuel supply in favour of coal–fuel oil mixtures [1]. These mixtures can be more easily pumped to burners and give higher combustion effectiveness, provided that proper promoters are added to the fuel [2].

In Italy, the national electricity board (ENEL) has carried out the above fuel substitution to some extent in selected power plants. As environmental issues are becoming more and more relevant, the evaluation of the overall effectiveness of electric power generation by means of this new process requires the classification and characterization of the ash produced. This point is essential in view of environmental impact assessment.

Coal–fuel oil ash has not yet been classified as a waste. In fact, the European Waste Catalogue lists fuel combustion residues as fly ash from coal (code 10.01.02), fuel oil (code 10.01.04*) and emulsified hydrocarbons (code 10.01.13*). No entry is found for coal–fuel oil ash, and its classification should be necessary for management purposes. At least, it should be made clear whether it is hazardous (as fuel oil ash) or not (as coal ash). Furthermore, the extent to which it will be produced in the near future is likely to increase, and this makes classification an urgent issue.

It is well known that coal ash has enough good pozzolanic activity to be used as natural pozzolanas substitute for the

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manufacture of blended cements and concrete [3–8]. This possibility relies on the high silica content and the prevalent presence of amorphous fraction, which both favour coal ash reactivity against added lime to form calcium silicate hydrate (CSH) [9,10]. In addition, it was proved in previous work that the alumina contained in this ash is able to react with added lime and gypsum to give calcium trisulphoaluminate hydrate (TSH) [11]. This product is analogous to natural ettringite ($6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$) and adds to CSH improving the binding properties of the final product.

Due to the lack of coal–fuel oil ash characterization, it is not known whether or not the above useful properties of coal ash are retained by the waste under investigation. Concern about this is due to the fact that when submitted to chemical analysis, coal–fuel oil ash shows a significantly lower content of silica and a much higher content of magnesium oxide in comparison to coal ash. To make this important issue clear, coal–fuel oil ash has been characterized and tested in hydratory systems containing lime alone or lime–gypsum mixtures. Comparison with coal ash has been carried out too.

2. Materials and methods

The characterization of coal–fuel oil ash starts with chemical analysis. A small sample of the ash was melted with alkaline carbonates and then dissolved with hydrochloric acid. Aliquots of the resulting solution were then used for the determination of the content of metals by atomic absorption spectroscopy, silica by precipitation and gravimetry and sulphates by turbidimetry. The results are reported in Table 1 where a comparison is made with a typical coal ash. It is seen that both silica and alumina, the compounds that can be exploited for matter recovery due to their reactivity in

Table 1
Chemical composition of coal–fuel oil and coal ashes (wt%)

	Coal–fuel oil	Coal
Loss on ignition at 1050 °C	10.20	12.94
SiO_2	35.68	42.74
MgO	11.84	2.12
Al_2O_3	11.47	28.49
Fe_2O_3	9.47	4.61
Na_2O	3.25	0.59
K_2O	1.38	0.81
CaO	0.45	3.72
MnO	0.32	–
CuO	0.21	–
NiO	0.15	–
PbO	0.14	–
Cr_2O_3	0.13	–
ZnO	0.04	–
CoO	0.02	–
CdO	5×10^{-3}	–
TiO_2	–	1.47
SO_4^{2-}	14.75	0.75
Total	99.50	98.27

Table 2
Cumulative amounts of metals released (mg/l)

	Ba	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
Coal–fuel oil ash	88.4	–	38.6	46.5	0.2	0.2	–	3.7	0.3
Coal ash	137.5	–	15.3	24.2	0.3	0.2	0.5	8.8	0.4

hydratory systems containing lime and gypsum, are present in significantly lower content with regard to coal ash. Other differences are a much higher content of MgO and SO_4^{2-} and a very little content of CaO.

The two types of ashes have also been characterized from the point of view of release behaviour. To this scope, the Italian dynamic basic waste characterization leaching test has been employed [12]. This test makes use of distilled water in 5:1 weight ratio with renewals at 2, 8, 24, 48, 72, 102, 168 and 384 h (16 days). Liquid–solid separation is carried out by filtration with 45 μm paper filter. The amounts released after each leaching step are summed to get cumulative final values. These results, relative to heavy metals, are reported in Table 2 and show that, from the point of view of leaching behaviour, coal–fuel oil ash is very similar to coal ash. This implies that in Italy coal–fuel oil ash could be addressed towards matter recovery as well as coal ash.

Coal–fuel oil ash has been tested for hydration behaviour in hydratory systems containing lime alone or lime and gypsum. The compositions of all the systems tested are reported in Table 3. Hydration was carried out at 25 and 40 °C and 100% R.H. for times ranging from 1 to 28 days. Cylindrical samples of size $d \times h = 2 \times 3\,cm^2$ were prepared for each experimental condition. At any hydration, time hydration was stopped by grinding the sample under acetone and then drying with diethyl ether. Stopped samples were stored in a desiccator. Hydration kinetic was studied testing stopped samples by means of quantitative determination of chemically combined water and reacted lime. The former was obtained by loss on ignition (LOI) at 1050 °C, while the latter by extraction and titration of residual lime according to the Franke method [13]. Hydrated samples were also qualitatively characterized by means of simultaneous thermogravimetric and differential thermal analysis (TGA/DTA). The scope was the identification of new phases formed upon hydration.

Cubic samples of 4 cm size were prepared and cured 28 days for the determination of unconfined compressive

Table 3
Compositions of the systems tested (wt%)

System	Coal–fuel oil ash	Lime	Gypsum	W/S[a] ratio
AL_H	60	40	–	0.43
AL_L	70	30	–	0.50
$AL_H G_L$	60	32	8	0.43
$AL_H G_H$	60	27	13	0.43
$AL_L G_L$	70	24	6	0.50
$AL_L G_H$	70	20	10	0.50

[a] Water to solid ratio.

strength (UCS). Three replicates of this measurement were carried out for each hydrated system.

3. Results and discussion

Fig. 1 shows the results of DTA for the system coal–fuel oil ash/lime AL_H hydrated at 40 °C. The formation of calcium silicate hydrate is visible as early as after 1-day-hydration (small endothermic peak at about 100 °C). This peak grows significantly at 28-days-hydration. Correspondingly, lime is strongly consumed (endothermic peak at about 450 °C). The endothermic peaks at about 800 °C are due to the decomposition of calcium carbonate. This is produced at lower temperature by reaction of unreacted lime with carbon dioxide formed by oxidation of unburned coal–fuel oil mixture.

The same qualitative results have been obtained for the system AL_H hydrated at 25 °C, as well as for the system AL_L hydrated at both 25 and 40 °C, in agreement with the hydration behaviour of similar systems containing coal ash instead of coal–fuel oil ash [11,14].
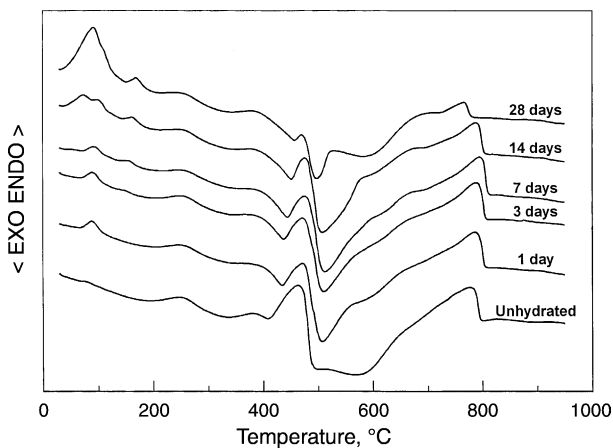

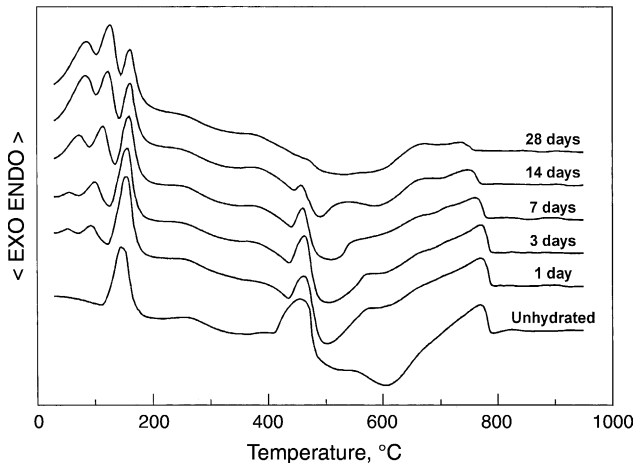Fig. 1. Thermograms of samples of system AL_H hydrated at 40 °C.

Fig. 2. Thermograms of samples of system AL_HG_L hydrated at 40 °C.
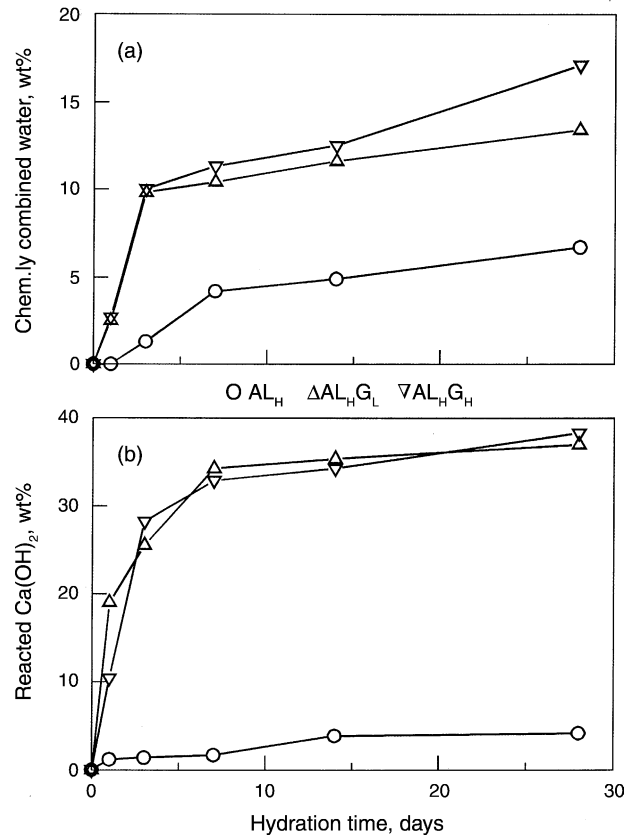

Fig. 3. Kinetics of hydration of system containing 60% ash at 25 °C: (a) above; (b) below.

Fig. 2 shows the results of DTA for the system coal–fuel oil ash/lime/gypsum AL_HG_L hydrated at 40 °C. In this case, the hydration products are calcium silicate hydrate (endothermic peaks of intensity increasing with hydration time at about 100 °C) and calcium trisulphoaluminate hydrate (endothermic peaks of increasing intensity at 120–130 °C). The consumption of lime and gypsum is clearly seen. The sequence of endotherms of decreasing intensity at about 450 °C is due to unreacted lime; the sequence of endotherms of equally decreasing intensity at about 150 °C is due to unreacted gypsum.

Again, these qualitative results are confirmed in other experimental condition of temperature and composition of the systems containing lime and gypsum. Furthermore, these systems behave similarly to systems containing coal ash instead of coal–fuel oil ash [11–14].

Quantitative data of reactivity in terms of chemically combined water are reported in Fig. 3a for the systems containing 60% ash, that is AL_H, AL_HG_L and AL_HG_H, cured at 25 °C. It is clearly seen that the presence of gypsum strongly increases the observed amount of chemically combined water. In fact, the values for the systems AL_HG_L and AL_HG_H are more than twice as-much-as those for the system AL_H. The positive effect of gypsum on hydration is confirmed by the highest values of chemically combined water observed in the case of the system AL_HG_H, richest in gypsum. This result is obviously

due to the formation of TSH beside CSH. The former, in fact, forms with a much higher content of crystallization water. The results of reacted lime are reported in Fig. 3b and show an even greater positive effect of gypsum on lime conversion in the systems containing 60% ash cured at 25 °C. In fact, in this case a nearly seven-fold increase of reacted lime is observed when gypsum is added to the ash–lime mixture.

Differently from chemically combined water, no significant difference is found in lime consumption between the two systems containing gypsum in different amounts (AL_HG_L and AL_HG_H).

At 25 °C the systems richer in ash behave slightly better from the point of view of the amount of chemically combined water. In fact, the 28-day values were found 8, 18.1 and 25.7% for the systems AL_L, AL_LG_L and AL_LG_H, respectively.

The behaviour of the above systems in relation to reacted lime was not the same. The effect of increased content of ash was positive for the system AL_L. In fact, the 28-day value of reacted lime was 14% in this case. On the other hand, the conversion of lime was found lower in the case of the system richer in ash containing gypsum. In fact, the values found for the systems AL_LG_L and AL_LG_H were 22.7 and 18.4%, respectively.

The reason for this may be due to the fact that the main hydration products, CSH and TSH, formed by two independent reactions whose kinetics may well be such that their relative rates depend on the composition of the reacting system.

Quantitative data at 40 °C are reported in Fig. 4a and b for the systems AL_L, AL_LG_L and AL_LG_H. These figures make it clear that hydration is strongly favoured at this higher temperature. The values of both chemically combined water (Fig. 4a) and reacted lime (Fig. 4b) are much higher than at 25 °C. Furthermore, carrying out the hydration at 40 °C strongly reduces the effect of composition. In fact, the quantitative data of both chemically combined water and reacted
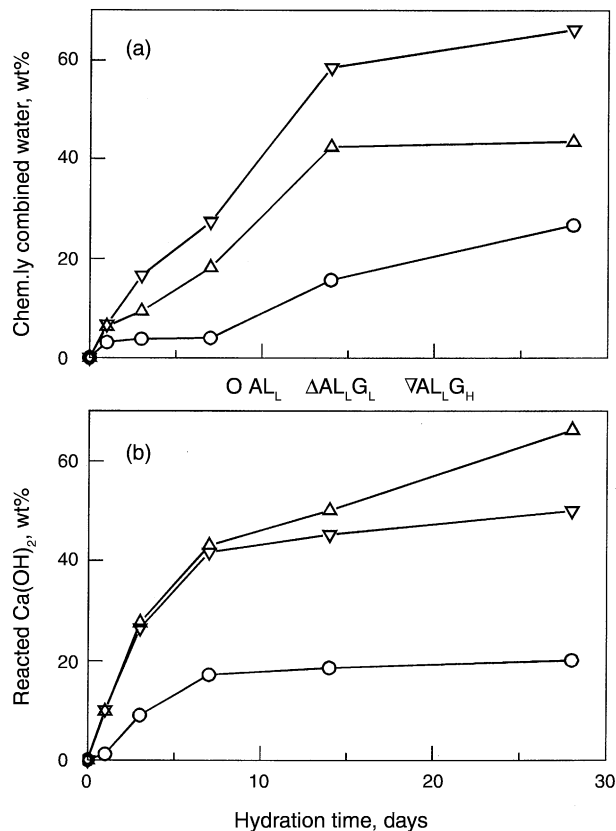

Fig. 4. Kinetics of hydration of system containing 70% ash at 40 °C: (a) above; (b) below.

lime were found almost independent of composition at 40 °C.

The effect of composition and temperature on reactivity is outlined in Tables 4 and 5 where the quantitative data of chemically combined water and reacted lime are reported for all the systems studied.

Table 4
Chemically combined water (wt%)

Hydration time (days)	AL_H (°C)		AL_L (°C)		AL_HG_L (°C)		AL_HG_H (°C)		AL_LG_L (°C)		AL_LG_H (°C)	
	25	40	25	40	25	40	25	40	25	40	25	40
1	0.0	2.0	0.0	3.1	2.6	1.2	2.7	5.9	10.3	6.3	12.6	6.7
3	1.3	2.0	0.0	3.8	9.9	3.1	10.0	6.9	11.3	9.4	14.3	16.6
7	4.2	2.9	1.1	4.0	10.4	12.4	11.3	13.8	16.1	18.2	20.5	27.4
14	4.9	11.6	6.5	15.7	11.6	25.7	12.5	25.6	17.6	42.4	20.9	58.5
28	6.7	23.4	8.0	26.7	13.4	38.6	17.1	44.8	18.1	43.4	25.7	66.1

Table 5
Reacted lime (wt%)

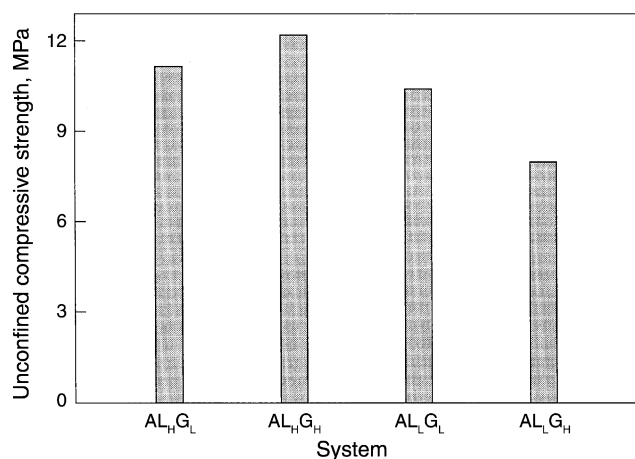| Hydration time (days)	AL_H (°C)		AL_L (°C)		AL_HG_L (°C)		AL_HG_H (°C)		AL_LG_L (°C)		AL_LG_H (°C)	
	25	40	25	40	25	40	25	40	25	40	25	40
1	1.2	7.1	4.5	1.2	19.0	13.5	10.4	10.6	10.8	9.8	4.8	10.1
3	1.4	7.9	5.4	9.0	25.5	25.8	28.2	24.8	15.4	27.6	10.1	26.5
7	1.7	9.0	5.7	17.2	34.3	38.7	32.9	32.1	21.8	43.0	17.0	41.6
14	3.9	13.0	10.1	18.6	35.4	43.4	34.3	39.4	22.1	50.1	17.1	45.2
28	4.2	14.9	14.0	20.1	37.0	54.5	38.3	61.6	22.7	66.2	18.4	50.0

Fig. 5. Mechanical strength of systems ash–lime–gypsum, hydrated at 40 °C.

A final remark on the quantitative aspects of hydration regards the comparison with systems containing coal ash instead of coal–fuel oil ash [11,14,15]. Although the composition of the systems studied in the papers referred to above was not exactly the same as that of the systems under investigation, it is possible to say that coal–fuel oil ash behaves very closely to coal ash when hydrated in mixtures containing lime and gypsum. This is a remarkable result in as-much-as coal–fuel oil ash has a less favourable chemical composition. As previously emphasized, when compared to coal ash, it shows lower amounts of both silica and alumina, that are required, in the presence of lime and gypsum, for the formation of the main hydration products CSH and TSH.

From the point of view of UCS, best results were obtained with the system coal–fuel oil ash/lime/gypsum. In these conditions, the mechanical properties take advantage from the formation of TSH beside CSH. The values of UCS found at 40 °C are reported in Fig. 5. They are of the order of magnitude that can be expected with hardened products made from by-products and industrial process wastes [16]. Furthermore, they are high enough to envisage the potential manufacture of pre-formed building blocks. According to Italian rules, concrete blocks that give at least 95% of strength determinations greater than 12 MPa for cubic samples 15 cm in size or 15 MPa for cylindrical samples 10 cm in diameter and 15 cm in height are classified as belonging to class C12/15.

A direct comparison between the experimental UCS results and the reference strength cannot be made because the specimens are different in size and in composition (paste for test blocks and concrete for reference blocks). Despite this, the strength data are of interest as starting point for the development of suitable building blocks because binder composition optimization and concrete mix design are useful tools available for technological improvement.

The effectiveness of binders based on CSH/TSH for environmental applications has been recently demonstrated by Péra et al. in a paper on valorization of automotive shredded residue in building materials [17].

4. Conclusions

The work carried out in this paper shows that coal–fuel oil ash has potentiality for an environmentally and technologically sound application for the manufacture of pre-formed building blocks. This is proved not only by the raw experimental results, but also by their comparison with those obtained with similar systems containing coal ash.

From the environmental point of view, the release of heavy metals was found very similar to that of typical coal ash.

From the chemical point of view, the main hydration products were the same as those formed in similar systems containing coal ash, i.e. calcium silicate hydrate and calcium trisulphoaluminate hydrate. Furthermore, the kinetics of hydration was similar too.

From the technological point of view, the results of UCS measurements showed that the systems studied are suited for the manufacture of classified building blocks at 40 °C.

References

[1] U.S. Department of Energy, Power Technology 2003 Databook, 2003, Online version, web site:http://nrel.gov/analysis/power_databook/.

[2] J. Choung, Z. Xu, J. Szymanski, An integrated approach for coal tailings management, Can. J. Chem. Eng. 78 (4) (2000) 780–785.

[3] H.F.W. Taylor, Cement Chemistry, Thomas Telford Publishing, London, UK, 1997.

[4] M.A. Abd. El-Aziz, The influence of addition of fly ash on the properties of ordinary Portland cement pastes of mortars, Silicages Industriels 68 (5–6) (2003) 69–79.

[5] C. Pok-Kie, K. Yun Ju, Pozzolanic properties of fly ash from a coal fired power plant, J. Korean Ceram. Soc. 40 (7) (2003) 702–708.

[6] G.C. Isaia, A.L.G. Gastaldini, R. Moraes, Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete, Cem. Concr. Composites 25 (1) (2003) 69–76.

[7] S.A. Khadilkar, M.W. Karandikar, R.M. Cursetji, Assessment of pozzolanic reactivity—an attempt on formulating a pozzolanic index, in: Proceedings of the 11th International Congress Chem. Cem, Durban, South Africa, 2003, pp. 868–877.

[8] M. Kobojakawa, S. Hanehara, K. Hwang, F. Tomosawa, Pozzolanic reaction of fly ash cement system, in: Proceedings of the 11th International Congress Chem. Cem, Durban, South Africa, 2003, pp. 736–746.

[9] R. Sersale, V. Sabatelli, G.L. Valenti, Structure et caracterisation del pouzzolanes et des cendres volantes, in: 7th International Congress Chem. Cem., vol. 4, 1980, Paris, France, 1980, pp. 546–549.

[10] H.J.H. Brouwers, R.J. Van Eijk, Chemical reaction of fly ash, in: Proceedings of the 11th International Congress Chem. Cem, Durban, South Africa, 2003, pp. 791–800.

[11] L. Santoro, I. Aletta, G.L. Valenti, Hydration of mixtures containing fly ash, lime and phosphogypsum, Thermochim. Acta 98 (1986) 71–78.

[12] Decree of Environment Ministry, 5 February 1998.

[13] F.A. Shebl und, U. Ludwig, Untersuchungen zur Bestimmung des Calciumhydroxids nach der Franke-Methode, Zement-Kalk-Gips 10 (1978) 510–515.

[14] G.L. Valenti, R. Cioffi, L. Santoro, S. Ranchetti, Influence of chemical and physical properties of Italian fly ashes on reactiv-

ity towards lime, phosphogypsum and water, Cem. Concr. Res. 18 (1988) 91–102.

[15] G.L. Valenti, R. Cioffi, R. Sersale, Production and utilization of fly ash in Italy, in: V.M. Malhotra (Ed.), ACI Special Publication 91, Proceedings of the 2nd International Conference Fly Ash, Silica Fume, Slag and Natural Pozzolan in Concrete, vol. 1, Madrid, Spain, 1986, Detroit, Michigan, USA, pp. 741–762.

[16] J. Berekta, R. Cioffi, L. Santoro, G.L. Valenti, Cementitious mixtures containing industrial process wastes suitable for the manufacture of pre-formed building elements, J. Chem. Tech. Biotechnol. 59 (1994) 243–247.

[17] J. Péra, J. Ambroise, M. Chabannet, Valorization of automotive shredded residue in building materials, Cem. Concr. Res. 34 (2004) 557–562.